PB83-238683

Full-Scale Utility FGD (Flue Gas Desulfurization) System Adipic Acid Demonstration Program. Volume 1 Process Results

Radian Corp., Austin, TX

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

Jun 83

U.S. Department of Commerce
National Technical Information Service
NTIS

PB83-238683

EPA-600/7-83-035a
June 1983

FULL-SCALE UTILITY FGD SYSTEM
ADIPIC ACID DEMONSTRATION PROGRAM:
VOLUME I - PROCESS RESULTS

by:

O.W. Hargrove, Jr.
J.D. Colley
R.L. Glover
M.L. Owen

Radian Corporation
8501 Mo-Pac Blvd.
Austin, Texas 78759

EPA Contract No. 68-02-3191

Project Officer:

J. David Mobley
Emissions Effluent Technology Branch
Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, NC 27711

Prepared for:

U.S. Environmental Protection Agency
Office of Research and Development
Washington, DC 20460

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-83-035a	2.	3. RECIPIENT'S ACCESSION NO. PB83 238683
4. TITLE AND SUBTITLE Full-scale Utility FGD System Adipic Acid Demonstration Program: Volume I. Process Results		5. REPORT DATE June 1983
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) O. W. Hargrove, Jr., J. D. Colley, R. L. Glover, and M. L. Owen		8. PERFORMING ORGANIZATION REPORT NO. DCN 82-213-012-36
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation 8501 Mo-Pac Boulevard Austin, Texas 78766		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-02-3191
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 6/80 - 11/82
		14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is J. David Mobley, Mail Drop 61, 919/541-2578. EPA-600/7-83-035b is Volume II. Continuous Emissions Monitoring Results.

16. ABSTRACT The report culminates a series of projects sponsored by the EPA, investigating the use of adipic acid as an additive to enhance SO2 removal in aqueous flue gas desulfurization (FGD) systems, using limestone reagent. A 9-month program at the 194-MW Southwest Power Plant (SWPP) of City Utilities, Springfield, MO, demonstrated the effectiveness of adipic acid and dibasic acids (the latter, by-products of the production of adipic acid). The program examined the effect of adipic acid addition on a limestone FGD system under natural and forced-oxidation modes of operation. Major conclusions are: (1) adipic acid addition is a feasible method for improving SO2 removal in systems that are limited by soluble alkalinity in the scrubber slurry feed; (2) the correlation from TCA prototype testing at Shawnee by TVA adequately predicts full-scale system performance for SO2 removal as a function of adipic acid concentration and pH; (3) limestone utilization can be improved with adipic acid addition because a lower scrubber feed can be used for a given SO2 removal; (4) increased limestone utilization from the addition of adipic acid can improve system reliability by reducing the accumulation of precipitating solids; and (5) dibasic acids are an equivalent alternative to adipic acid, and also the least expensive alternative examined to meet SWPP's SO2 removal requirement.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Calcium Carbonates	Pollution Control	13B 07B
Adipic Acid	Dibasic Organic Acids	Stationary Sources	07C
Flue Gases			21B
Desulfurization			07A, 07D
Scrubbers			13I
Limestone			08G

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

This report is the culmination of a series of projects sponsored by the Environmental Protection Agency investigating the use of adipic acid as an additive to enhance sulfur dioxide (SO_2) removal in aqueous flue gas desulfurization systems using limestone reagent. A nine-month demonstration program was performed at the 194 MW Southwest Power Plant of City Utilities, Springfield, MO, demonstrating the effectiveness of adipic acid, and dibasic acid, a by-product obtained during production of adipic acid. The test program examined the effect of adipic acid addition to a limestone FGD system under natural and forced oxidation modes of operation.

The major conclusions obtained are as follows: (1) adipic acid addition is a feasible method for improving SO_2 removal in systems that are limited by soluble alkalinity in the scrubber slurry feed; (2) the correlation from TCA prototype testing at Shawnee by TVA adequately predicts full-scale system performance for SO_2 removal as a function of adipic acid concentration and pH; (3) limestone utilization can be improved with adipic acid addition because a lower scrubber feed can be used to achieve a given SO_2 removal; (4) increased limestone utilization from the addition of adipic acid can improve system reliability by reducing the accumulation of precipitating solids, especially in forced oxidized systems; and (5) the performance of dibasic acid provides an equivalent alternative to the use of adipic acid and was also the least expensive alternative examined for the SWPP to meet their SO_2 removal requirement.

This report is submitted in fulfillment of Contract Number 68-02-3191 by Radian Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from January 1981 to September 1981. The final report was completed in November, 1982.

CONTENTS

Abstract iii
Figures vi
Tables vii

Section 1 - Summary 1
1.1 Background 1
1.2 Program Objectives 3
1.3 Process Description 5
1.4 Forced Oxidation Test Results 8
1.5 Natural Oxidation Test Results 13
1.6 Adipic Acid Consumption 16
1.7 Operating Characteristics 18
1.8 DBA Testing 23
1.9 Solid Waste Testing 25
1.10 Economics 26
1.11 Conclusions 27

Section 2 - Introduction 30
2.1 Background 30
2.2 Program Goals 32

Section 3 - FGD System Description 34
3.1 Limestone Preparation Facility 37
3.2 Scrubber Modules 37
3.3 Solids Dewatering 38
3.4 Adipic Feed System 39
3.5 Forced Oxidation 40
3.6 Continuous Monitoring 41

Section 4 - Data Acquisition 42
4.1 Process Characterization 42
4.2 Continuous Emissions Monitoring Systems 50
4.2.1 Continuous Monitoring Equipment 51
4.2.2 Certification of Continuous Emissions Monitoring Systems 53
4.3 Quality Assurance Program 56
4.3.1 Quality Assurance (QA) for Analytical Data 58
4.3.2 Quality Assurance for Continuous Emissions Monitoring Data 59
4.3.3 Quality Assurance for Process Instrumentation Readings . . . . . .

Section 5 - Forced Oxidation Test Phase 62
5.1 Forced Oxidation Equipment 62
5.2 Forced Oxidation Test Plan 63
5.3 Forced Oxidation Test Results 66

5.3.1 SO_2 Removal Efficiency 66
5.3.2 Limestone Utilization 76
5.3.3 Sulfite Oxidation 77
5.3.4 Sulfite Blinding 79
5.3.5 Chemical Scaling 80
5.3.6 Adipic Acid Consumption 82

Section 6 - Natural Oxidation Test Phase 85
6.1 Test Plan 85
6.2 Test Results 86
6.2.1 SO_2 Removal 87
6.2.2 Limestone Utilization 95
6.2.3 Sulfite Blinding 98
6.2.4 Chemical Scaling 99
6.2.5 Adipic Acid Mass Balance 101

Section 7 - Dibasic Acid Test Phase 104
7.1 Test Plan 104
7.2 DBA Test Results 105
7.2.1 SO_2 Removal 105
7.2.2 Limestone Utilization and Sulfite Oxidation 108
7.2.3 Chemical Scaling 109
7.2.4 Dibasic Acid Mass Balance 109

Section 8 - Equipment Performance 112
8.1 System Reliability 112
8.1.1 Forced Oxidation 115
8.1.2 Natural Oxidation 119
8.1.3 DBA Testing 123
8.2 Equipment Limitation and Modification 125
8.2.1 Forced Oxidation 126
8.2.2 Natural Oxidation 128
8.2.3 DBA Testing 129
8.3 Physical Examination of Scrubbers 130
8.3.1 Forced Oxidation 131
8.3.2 Natural Oxidation 132
8.3.3 DBA Testing 133

Section 9 - Cost Analysis of Options To Improve SWPP Scrubber SO_2 Removal Efficiency 135

Section 10 - Solid Waste Testing 140
10.1 Fermentation 140
10.2 Bioassy Tests 141
10.2.1 Mutagenicity Evaluation 143
10.2.2 Cyotoxic Evaluation 147
10.2.3 Acute Toxicity 151
10.3 Leaching Results 154

References 157

Appendix A - Laboratory Protocol/Quality Assurance Results A-1

Appendix B - Buffer Titration for Limestone Slurries Containing Carboxylic Acids B-1

Appendix C - Process and Analytical Data Plots C-1

Appendix D - Cost Analysis of Options to Upgrade C.U.'s Southwest Unit No. 1 Scrubbing System D-1

Appendix E - Mutagenicity Evaluation of Solid FGD Sludge Samples in the EPA Level 1 Ames Salmonella/ Microsome Plate Test . . . . . E-i

Appendix F - Cytotoxic Evaluation of Solid FGD Sludge Samples in the EPA Level 1 Rodent Cell (CHO) Clonal Toxicity Assay . . . . . F-i

Appendix G - Toxic Evaluation of Solid FGD Sludge Samples in the EPA Level 1 Daphnia Magna Toxicity Assay . . . . G-i

FIGURES

Number		Page
1-1	Southwest unit scrubber module flow diagram	1
1-2	Fit of Springfield data to revised Bechtel model	12
1-3	Fit of Springfield tray tower data to model	17
1-4	Comparison of alternatives for meeting 85% removal at Springfield	28
3-1	Southwest Unit 1 FGD flow scheme	36
4-1	Location of continuous monitors and sample ports	52
4-2	Certification testing schedule	54
5-1	Summary of SO_2 removal for forced oxidation/adipic acid testing in Module S-1	67
5-2	Summary of SO_2 removal for forced oxidation/adipic acid testing in Module S-2	68
5-3	Results of testing without TCA spheres	71
5-4	Fit of Springfield data to Shawnee predictive model	74
6-1	Summary of natural oxidation/adipic acid testing - Module S-1	88
6-2	Summary of natural oxidation/adipic acid testing - Module S-2	89
6-3	Fit of Springfield tray tower data to model	94
6-4	Percent limestone utilization versus scrubber feed pH - without adipic acid	96
6-5	Percent limestone utilization versus scrubber feed pH - with adipic acid	97
8-1	Boiler, scrubber, and continuous monitor reliability during forced oxidation testing	116
8-2	Boiler and scrubber reliability during March and April (adipic acid testing)	117
8-3	Boiler, scrubber, and continuous monitor reliability during natural oxidation testing	120
8-4	Boiler, scrubber, and continuous monitor reliability during DBA testing	124
9-1	Cumulative present cost for Options 1, 2, 3, and 4	138
9-2	Cumulative present cost for Options 1A, 2A, and 3A	139
10-1	Rodent cell (CHO) clonal toxicity assay EC_{50} determination	150

TABLES

Number		Page
1-1	Summary of Forced Oxidation Testing	9
1-2	Summary of Natural Oxidation Testing	14
1-3	Adipic Acid Material Balance Results	19
1-4	Scrubber Reliability During Aidpic Acid Demonstration Program	21
1-5	DBA Test Results	24
3-1	Typical Coal Properties for C.U.'s Southwest Power Plant	35
4-1	Gas Phase Data Frequency of Measurements per Week	44
4-2	Liquid Phase Data Frequency of Measurements per Week	45
4-3	Slurry and Solid Phase Data Frequency of Measurements per Week	46
4-4	Hourly Process Data	47
4-5	Dart Hourly Report Format	55
4-6	Summary of Certification Testing at City Utilities Southwest Power Plant, Springfield, Missouri	57
5-1	Forced Oxidation Test Plan	64
5-2	Summary of SO_2 Removal During Forced Oxidation Testing	69
5-3	Days of Operation at Indicated SO_2 Removal Efficiency	72
5-4	Limestone Utilization During Forced Oxidation Testing	76
5-5	Sulfite Oxidation During Forced Oxidation Testing	78
5-6	Relative Saturation of Calcium Sulfate in Scrubbers	81
5-7	Adipic Acid Material Balance Results	83
6-1	Natural Oxidation Test Schedule	86
6-2	Summary of Natural Oxidation SO_2 Removal Results	90
6-3	Summary of Limestone Utilization Results	95
6-4	Adipic Acid Material Balance Results for the Natural Oxidation Testing	102
7-1	Average SO_2 Removal for DBA Testing	105
7-2	Limestone Utilization and Sulfite Oxidation During DBA Testing	108
7-3	DBA Material Balance Results	110
8-1	Boiler Scrubber, and Continuous Monitoring System Reliability During Adipic Demonstration Program	113
8-2	Summary of Changes to Improve FGD System Reliability	114
10-1	Fermentation Test Conditions and Results	142
10-2	Level 1 Bioassay Samples	141
10-3	Bioassay Results Summary	144
10-4	EC_{50} Values for Daphnia Magna of FGD Sludge Solids	153
10-5	RCRA Leachate Results	155
10-6	ASTM Leachate Results	156

SECTION 1

SUMMARY

The U.S. Environmental Protection Agency (EPA) has focused a portion of their research activities on developing organic-acid-enhanced aqueous flue gas desulfurization (FGD) technology using limestone reagent for existing and new facilities. In 1981, EPA sponsored a full-scale demonstration at City Utilities of Springfield's Southwest Power Plant (SWPP) with Radian Corporation employed as the test contractor. This report presents the results of that investigation.

1.1 BACKGROUND

The majority of aqueous FGD systems currently operated by the electric utility industry employ lime or limestone reagent. Lime/limestone FGD systems are also anticipated to be the most widely used technologies in the future because of lower capital and operating costs compared to other aqueous FGD technologies. Of the two, limestone systems are generally less costly since limestone is less expensive than lime. Although limestone systems are widely used, their performance has been limited by the reactivity of the reagent which produces a lower soluble alkalinity in the scrubber slurry. This limitation results in requirements for relatively higher liquid-to-gas (L/G) ratios and larger reaction tanks than other FGD scrubbing processes.

In response to these limitations, EPA's Industrial Environmental Research Laboratory at Research Triangle Park (IERL-RTP) embarked on a research and development program to improve the performance of lime/limestone systems. One of the most promising aspects of this effort has been the use of organic acids as buffering agents to increase soluble alkalinity in limestone FGD systems. Adipic acid was identified as a suitable additive because of its

physical properties, availability and cost. Recently, EPA has sponsored extensive laboratory-, pilot-, and prototype-scale studies on aidpic-acid-enhanced limestone systems. Initial testing indicated that addition of adipic to limestone FGD systems can provide one or more of the following process improvements:

- enhanced SO_2 removal,
- increased limestone utilization,
- lower capital and operating costs, and
- greater system flexibility.

The first three improvements are self-explanatory; the fourth requires some additional explanation. Limestone systems with adipic acid addition can be used successfully in a wider range of applications than systems using other additivies, and will result in a more flexible operating system. Consider, for example, that adipic acid enhances performance on both natural and forced oxidation systems while inorganic buffers are less effective in forced oxidation systems. A forced oxidation limestone system has been projected as a more attractive option compared to a natural oxidation system because of improved sludge disposal operations. However, soluble alkalinity can limit the SO_2 removal performance of limestone systems, and inorganic additives such as magnesium are ineffective in forced oxidized operations because of the low dissolved sulfite concentratins. Alternatively, adipic acid addition has been found to be effective in increasing soluble alkalinity in forced oxidized system. Another example to consider is the influence coal chloride content has on the effectiveness of additives. Relatively low levels of adipic acid have been effective in high dissolved chloride systems while greater amounts of magnesium are required to counteract the effects of chlorides. Therefore, adipic acid could be quite attractive in a plant where the coal chloride concentration varies significantly. These are only two examples of how adipic acid addition can be beneficial. Other advantages in flexibility include: (1) ability to respond to changes in coal sulfur content; (2) adaptability to changes in limestone reactivity; and (3) ability to achieve greater than 95 percent removal to aid in achieving 90 percent removal on a

rolling 30-day average basis. Reducing the limitations and increasing the flexibility of limestone systems will promote the use of limestone rather than lime which is more reactive but also more expensive.

The improvements resulting from adipic acid addition can be realized in new systems as well as in marginally designed existing systems experiencing performance limitations. Available data indicate that new adipic acid-enhanced systems can be designed to meet New Source Performance Standards at lower costs or to attain more stringent removal requirements to comply with local regulations. Existing systems which are not meeting design specifications can be easily adapted to accommodate adipic acid addition to improve SO_2 removal and/or limestone utilization. An excellent potential exists to use adipic acid as a less expensive alternative than other remedial actions.

More recently, diabasic acid (DBA) has been identified as a potentially less costly alternative to adipic acid. DBA, a by-product of adipic acid manufacturing, is a mixture of glutaric, adipic and succinic acids. Other by product organic acid containing streams may also be attractive options.

1.2 PROGRAM OBJECTIVES

Results of previous activities were sufficiently encouraging to warrant the demonstration of the use of organic additives in a full-scale limestone FGD system. The main objective of this program was to demonstrate the effectiveness of adipic acid to improve the performance of limestone systems. A second objective was to demonstrate the validity of the previously developed data base as a design tool for full-scale FGD systems. DBA addition was also briefly tested for comparison with the adipic acid data base. In meeting these objectives, SO_2 removal data was collected using monitors that were certified and operated according to EPA procedures.

The test program was influenced by the characteristics of the full-scale system where the demonstration was conducted. City Utilities of Springfield (C.U.) was willing to participate in the demonstration program because they had been actively pursuing methods to improve SO_2 removal in the limestone FGD system at their SWPP. The system had been unable to achieve design SO_2

removals and, consequently, was unable to meet permit requirements of 520 ng/J (1.2 lb $SO_2/10^6$Btu). This emission limit typically requires 82 to 85 percent SO_2 removal. Therefore, the test program primarily focused on the use of adipic acid to improve SO_2 removal.

Other factors also influenced the test program. The FGD system at SWPP is a natural oxidation system. However, EPA elected to also conduct forced oxidation tests since both natural and forced oxidation designs are feasible options for new and retrofit systems and adipic acid offers advantages in the forced oxidation system that inorganic enhancement agents (e.g., magnesium or sodium) do not provide. As a result of these considerations the following areas for testing were specified at SWPP:

- forced oxidation tests
  - baseline
  - adipic acid addition for 95 percent removal
- natural oxidation tests
  - baseline
  - adipic acid addition
    - -- 85 percent SO_2 removal
    - -- 95 percent SO_2 removal
  - DBA addition
    - -- 85 percent SO_2 removal
    - -- 95 percent SO_2 removal

The performance of the FGD system at 95 percent removal was investigated to determine the potential of organic acid addition to meet stringent SO_2 removal requirements. Since the SWPP system is a natural oxidation process, 85 percent removal was investigated in natural oxidation tests to assist City Utilities in identifying the operating conditions necessary to meet their permit requirements. DBA was also tested at 85 percent removal as a potentially less expensive option for the SWPP.

A total of nine months of testing was conducted at SWPP. Four months were spent at the beginning of the program investigating adipic acid addition in a forced oxidation system. Next, adipic acid addition to a naturally oxidized system to achieve 85 to 95 percent SO_2 removal was tested over a period of approximately three and one half months. Finally, DBA was tested in a naturally oxidized system for approximately one and a half months. Following a brief process description, the results of these testing efforts are summarized.

1.3 PROCESS DESCRIPTION

C.U.'s Southwest Unit 1 is a 194 MW unit designed to burn coal containing 3.5 to 4.0 percent sulfur. After exiting the boiler, flue gas passes through the air preheater, electrostatic precipitator, and induced draft fans prior to entering the FGD system and subsequently exiting the unit through the stack.

The original FGD system consisted of two parallel turbulent contact absorber (TCA) modules, each sized to handle 60 percent of the design flue gas flow. Three contact levels, each with 100 mm (4 inches) of TCA spheres were provided in each module. The L/G ratio at full load conditions was 6 to 7 ℓ/Nm^3 (40 to 45 gallons per 1000 acf). The pressure drop across the absorber portion of each module was 25 to 30 cm H_2O (10 to 12 inches H_2O). Prior to the demonstration program, C.U. had experienced reliability problems and excessive maintenance expenses with the TCA modules. During the course of the forced oxidation tests, the TCA spheres were removed from one of the modules (S-1) and some testing was conducted without the spheres. Then, the spheres were replaced for the remainder of forced oxidation testing. The module was converted to a tray absorber at the conclusion of the forced oxidation tests. The other module (S-2) was not converted to a tray absorber until the end of the demonstration program so that data were collected for both TCA and tray tower contactors during natural oxidation testing.

Figure 1-1 presents a flow schematic for one of the two modules. Flue gas enters the presaturator and is cooled by supernatant liquor (thickener overflow). The gas then passes through three levels where it is contacted by the slurry and SO_2 removal is accomplished. Entrained slurry is removed from the flue gas by the mist eliminator and the cleaned flue gas exits out the stack. The lower bank of mist eliminator blades is washed continuously with supernatant liquor to control slurry accumulation and scale formation.

The dewatering system consists of a thickener, a vacuum filter, and a pug mill for mixing ash with FGD sludge. The ash-sludge mixture is landfilled onsite. The thickener overflow is collected in the supernatant tank and returned to the system. The limestone preparation facility consists of a wet ball mill producing a relatively coarse slurry, 50 to 60 percent passing through 200 mesh. The ground limestone is collected in a sump, diluted, and them pumped to the limestone storage tank. During the demonstration, adipic acid was added into the limestone sump. Since the dewatering and limestone preparation equipment were common to both modules, the adipic acid concentration in each module could not be varied independently.

Two relatively simple modifications were made to the FGD system to accommodate the needs of the demonstration program: 1) an adipic acid feed system was installed and 2) forced oxidation capability was temporarily provided. UOP's Air Correction Division provided the equipment modifications. Both systems were designed for temporary use during the demonstration program and, as a result, suffered from the omission of some design features that would be included in permanent installations. In particular, the forced oxidation modifications were limited to the addition of air compressors and reaction tank spargers. No revisions were made to the dewatering system, which was originally designed for natural oxidation. The substantial change in sludge properties created some operating problems during forced oxidation tests. Also, the existing reaction tank agitator and gear box assembly was undersized for operation in the forced oxidation mode so that oxidation efficiencies were affected. The types of problems observed were attributable

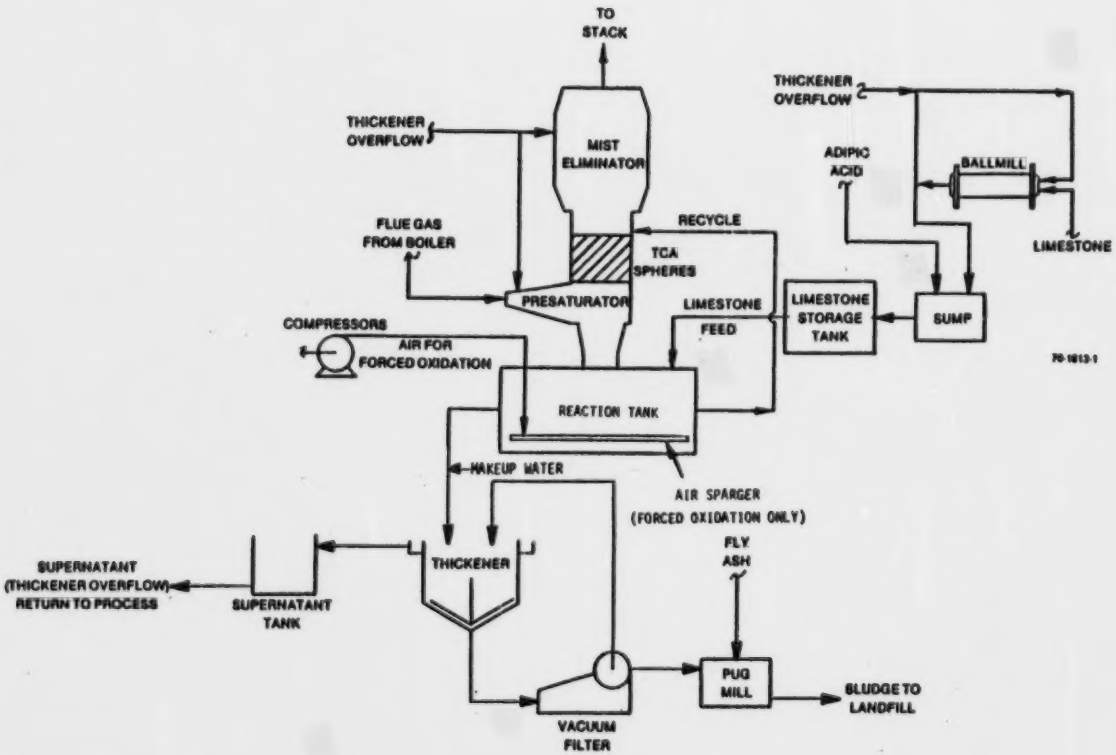


Figure 1-1. Southwest Unit 1 scrubber module flow diagram.

to retrofitting a natural oxidation system to test in a forced oxidation mode, and are not indicative of problems that would result from the use of adipic acid.

1.4 FORCED OXIDATION TEST RESULTS

Forced oxidation testing was conducted because it is a major design configuration for limestone FGD systems. Furthermore, forced oxidation systems produce waste sludge containing a smaller amount of occluded water than naturally oxidized systems. Test data collected prior to the demonstration program indicated that the small amount of water contained in the sludge would minimize the loss of adipic acid from the system.

Forced oxidation testing was initially conducted without adipic acid addition to provide baseline performance data. Then, adipic acid addition was initiated and the performance of both modules was monitored. The stringent SO_2 removal goal of 95 percent was established to provide a severe test of the ability of adipic acid to enhance removal performance. Since C.U. was interested in eliminating the TCA spheres from the system because of repeated failures, Module S-1 was operated for a short time with the TCA spheres removed, and the surfaces of the TCA cages provided the only gas-liquid contacting. The remainder of the forced oxidation tests were conducted with the TCA spheres restored to S-1. A summary of the results of the forced oxidation testing is presented in Table 1-1.

The results indicate that in tests without the TCA spheres, addition of adipic acid to about 1300 ppm in the slurry with a scrubber feed pH of 5.4 increased the SO_2 removal from less than 50 percent removal at baseline conditions to about 84 percent removal. These results represent the performance of a system limited by mass transfer area. In a one-day test effort to further increase SO_2 removal without the TCA spheres, the adipic acid level and pH were increased to 2000 ppm and 5.6, respectively. Over 90 percent SO_2 removal was achieved but the long-term operability of the system under these conditions was not demonstrated.

TABLE 1-1. SUMMARY OF FORCED OXIDATION TESTING

	Operating Time (Days)	Scrubber Feed pH	Adipic Acid (ppm)	Atoms O/ Mole SO_2 Removed	SO_2 Removal (%)	Limestone Utilization (%)	Sulfite Oxidation (%)
Testing Without TCA Spheres (Module S-1)							
Baseline	20	5.4	0	3.1	46	89	95
Adipic Acid Addition	6	5.4	1340	2.8	84	89	90
Testing With TCA Spheres							
Baseline - Module S-2	24	5.4	0	3.0	58	88	91
Adipic Acid Addition -							
Module S-2[a]	49(13)	5.0(5.0)	2410(3323)	3.0(3.2)	91(96)	92(92.5)	94(>99)
Module S-1	40	5.1	2340	1.3[b]	89	91	74[b]

[a]Average results are presented in the table. The results in parentheses represent performance after startup and shakedown problems had been resolved.

[b]Maintenance problems prevented efficient oxidation for Module S-1 compressors.

In testing conducted with TCA spheres, an average SO_2 removal of 91 percent was achieved in Module S-2 at an adipic acid concentration of 2410 ppm and a pH of 5.0. Similarly, an average SO_2 removal of 89 percent was obtained in Module S-1 with 2340 ppm of adipic acid and a pH of 5.1. This compares with a baseline SO_2 removal of only 58 percent at a higher pH of 5.4 It should be noted that Module S-1 could not be fully oxidized throughout the program due to continuing compressor maintenance problems. Therefore, the test data from S-1 are more indicative of a natural oxidation system experiencing high oxidation rates than a properly designed forced oxidized system.

Although the 95 percent average SO_2 removal goal was not achieved during the entire forced oxidation test period, it is significant that 90 percent average SO_2 removal and 90 percent limestone utilization were obtained over the 49 day test period. These average results included data collected during start-up and optimization periods when process operating difficulties such as limestone blinding with sulfite and process water discharge from the dewatering system were encountered and solved. These difficulties are primarily attributable to retrofitting the FGD system to accommodate forced oxidation as discussed earlier. During a two week period in April near the end of the forced oxidation, the average SO_2 removal in Module S-2 was 96 percent, and 95 percent daily average SO_2 removal was achieved on all but two days.

The dramatic increases in SO_2 removal with adipic acid addition in the forced oxidation tests were accomplished without a decrease in limestone utilization. Baseline test results with and without TCA spheres reveal a very good limestone utilization of 88 to 89 percent. Limestone utilization remained high when greater SO_2 removal was attained with adipic acid. In other applications where an improvement in SO_2 removal is not the primary concern, it is anticipated that limestone utilization could be improved by the addition of adipic acid while maintaining constant SO_2 removal. The improvement in limestone utilization would be due to the ability to operate at a lower pH with adipic acid addition.

The performance data collected from Modules S-1 and S-2 during the tests with TCA spheres were compared with data from a previous test program collected in a smaller prototype system. The adipic acid prototype testing was sponsored by EPA and conducted at the Tennessee Valley Authority's (TVA) Shawnee test facility during the 1978 to 1980 period. A correlation relating SO_2 removal with adipic acid concentration and pH was subsequently developed by Bechtel[1] based on the Shawnee prototype data base:

$$\text{Fractional } SO_2 \text{ Removal} = 1 - \exp\{-0.0047 \exp(pH + 0.00062\ Ad)\} \qquad (1\text{-}1)$$

where pH and Ad represent the pH of the scrubber feed liquor and adipic acid concentration in ppm, respectively.

The full-scale data collected at SWPP were correlated using the form presented in Equation 1-1 for pH values from 4.8 to 5.5 and adipic acid concentrations from 0 to 4000 ppm. The full-scale correlation is shown in equation 1-2.

$$\text{Fractional } SO_2 \text{ Removal} = 1 - \exp\{-0.00415 \exp(pH + 0.0065\ Ad)\} \qquad (1\text{-}2)$$

Figure 1-2 compares the predicted SO_2 removal using Equation 1-2 with observed results. Although the data scatter represent both the operational problems discussed previously and the fluctuations of a full-scale system, 90 percent SO_2 removal was routinely achieved with an adipic acid concentration of 2000 ppm and a scrubber feed pH of 5.0.

The Shawnee (prototype) correlation predicts SO_2 removals which are 2 to 5 percent greater on the average than the actual results observed on the full-scale system at SWPP. Some differences in the Shawnee and SWPP FGD systems which could contribute to the difference in correlation include: 1) a slightly lower TCA sphere charge at SWPP, 2) slightly lower slurry and gas rates on an equivalent cross-sectional area basis at SWPP, and 3) coarser

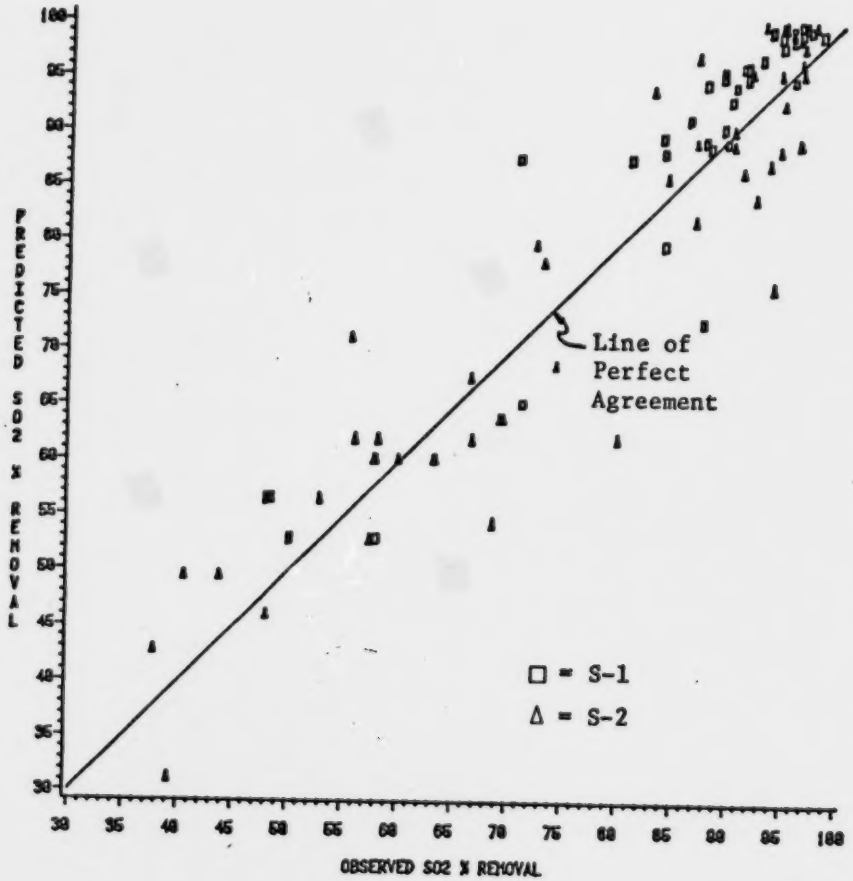


Figure 1-2. Fit of springfield data to revised Bechtel model.
Removal = 1 - exp{-0.00415 exp(pH + 0.00065 Ad)}

limestone at SWPP. Significant maldistribution of TCA spheres observed at the end of the forced oxidation testing at SWPP would also contribute to the difference. The conclusion that can be drawn from this comparison is that the Shawnee data base can be used as an effective design tool for full-scale systems. Good engineering practice would require consideration of important variables affecting performance that are not included in Equation 1-1 or the application of some conservatism when predicting system performance.

1.5 NATURAL OXIDATION TEST RESULTS

After a one month scheduled outage following the forced oxidation testing, investigation of FGD system performance in the natural oxidation mode was initiated. During the outage, Module S-1 had been converted to a tray tower; however, the resulting tray pressure drop was initially too small. The tray void area was reduced to increase the gas-side pressure drop to specified levels (i.e., 10 to 12 inches across the absorber) after about 6 weeks of natural oxidation testing.

Much of the testing in the natural oxidation mode focused on defining conditions required to meet 85 percent SO_2 removal since City Utilities was interested in gaining experience in operating the FGD system under conditions required to meet their SO_2 emission limitation. Additionally, some testing was conducted to achieve 95 percent SO_2 removal and to determine the operating conditions required to meet more stringent SO_2 emission limits. The natural oxidation results are summarized in Table 1-2 for both the TCA and tray towers.

After baseline testing was conducted, adipic acid addition was initiated to achieve 85 percent SO_2 removal. Initially, screening tests were performed by varying the pH and adipic acid concentration independently and observing the resulting SO_2 removal. The results of these screening tests were then used to select preferred operating conditions for longer term tests at constant

TABLE 1-2. SUMMARY OF NATURAL OXIDATION TESTING

	Operating Time (Days)	pH	Adipic Acid Conc. (ppm)	SO_2 Removal (%)	Limestone Utilization (%)
Tray Tower (S-1)					
Baseline[a]	24	5.6	0	68	79
Goal - 85% Removal[a] (Screening)	17	5.4	1000	87	81
Goal - 85% Removal (5.2 pH)	12	5.2	760	90	86
Goal - 85% Removal (5.5 pH)	10	5.5	640	91	-
Goal - 95% Removal	17	5.4	1750	96	78
TCA Tower (S-2)					
Baseline	24	5.6	0	72	69
Goal - 85% Removal (Screening)	17	5.3	890	91	92
Goal - 85% Removal (5.2 pH)	12	5.2	700	88	82
Goal - 85% Removal[b] (5.5 pH)	10	5.4	550	78	75
Goal - 95% Removal[b]	13	5.2	1690	94	86

[a] The void area in the tray tower was about 10 percent higher during these test periods than in the later test periods.

[b] These goals were obtained in the tray module but not in the TCA module. The goals for the TCA module were not attained due to deteriorating conditions in the TCA module and a common adipic acid addition system which prevented independent control of adipic acid levels.

pH and adipic acid concentrations. The longer term steady-state tests were conducted at a pH of 5.5 which was the setpoint typically used at SWPP, and a pH of 5.2 which approached the pH recommended by EPA for reducing adipic acid consumption. Approximate adipic acid addition rates for these pH's were estimated from the screening tests.

Subsequent test results in the tray tower produced an average 90 percent SO_2 removal at a pH of 5.2 and an adipic acid concentration of 760 ppm. An average SO_2 removal of 91 percent was achieved at a pH of 5.5 and an adipic acid concentration of 640 ppm. The data were collected by continuous emission monitors and represent average performance during periods of fluctuating plant load. The SO_2 removal achieved at full load was approximately 85 percent at each pH level tested. Test results also show that 95 percent SO_2 removal at full load condition was achieved with 1700 to 1800 ppm adipic acid at a pH of 5.4.

The results for the TCA module show that the performance of the system deterioriated over the course of the natural oxidation testing period. Note that only 78 percent removal was achieved in the TCA compared to 91 percent removal in the tray tower during the third set of tests with an 85 percent removal goal. Plugging in the TCA was at least partially responsible for the decline in performance and illustrates the type of problems encountered previously at the SWPP. A more detailed discussion of these problems will be presented later in this section.

The results for limestone utilization presented in Table 1-2 indicate that an improvement was observed in the adipic acid tests compared to the baseline tests. The primary reason for the improvement is that adipic acid addition allows the desired SO_2 removal to be obtained at a lower pH which, in turn, increases limestone utilization.

Since one module had been converted to a tray tower and the TCA module suffered from operating difficulties which reduced performance efficiency, it is difficult to compare the SWPP full-scale results directly with the

Shawnee TCA prototype results for natural oxidation. Most of the correlations reported for prototype natural oxidation testing were derived for higher pH levels than at SWPP. However, spot checks of full-scale data obtained at higher pH levels before the TCA module performance deteriorated indicate that the Shawnee correlations predict full-scale performance results reasonably well. As in the forced oxidation test series, the prototype correlations for natural oxidation tests predict slightly higher SO_2 removals than achieved in the full-scale system.

The data collected in the demonstration program from the full-scale tray tower were fit to the following equation:

$$\text{Fractional } SO_2 \text{ Removal} = 1 - \exp\{-0.00131Ad - 0.00216\exp(pH) - 0.00996L/G\} \quad (1\text{-}3)$$

The L/G ratio is expressed in units of gallons per thousand cubic feet of gas. Note that the effects of liquid and gas rates resulting from load changes could be observed and correlated to SO_2 removal during the natural oxidation testing. The wider range of SO_2 removals observed during the natural oxidation tests compared to the narrow range resulting from the forced oxidation removal goal of 95 percent permitted the effect of L/G to be observed.

The agreement between actual SO_2 removal and the removal predicted by Equation 1-3 is presented in Figure 1-3. This equation was developed to describe the trends noted during the program. Caution should be applied in using the equaiton for design purposes, especially for extrapolation beyond the conditions tested at the full-scale system.

1.6 ADIPIC ACID CONSUMPTION

Aidpic acid which is added to a limestone FGD system can leave the system by several mechanisms: 1) soluble adipic acid which is lost in the water occluded with the solids of the scrubber sludge, 2) adipic acid that is coprecipitated with the solids in the sludge, 3) adipic acid which is

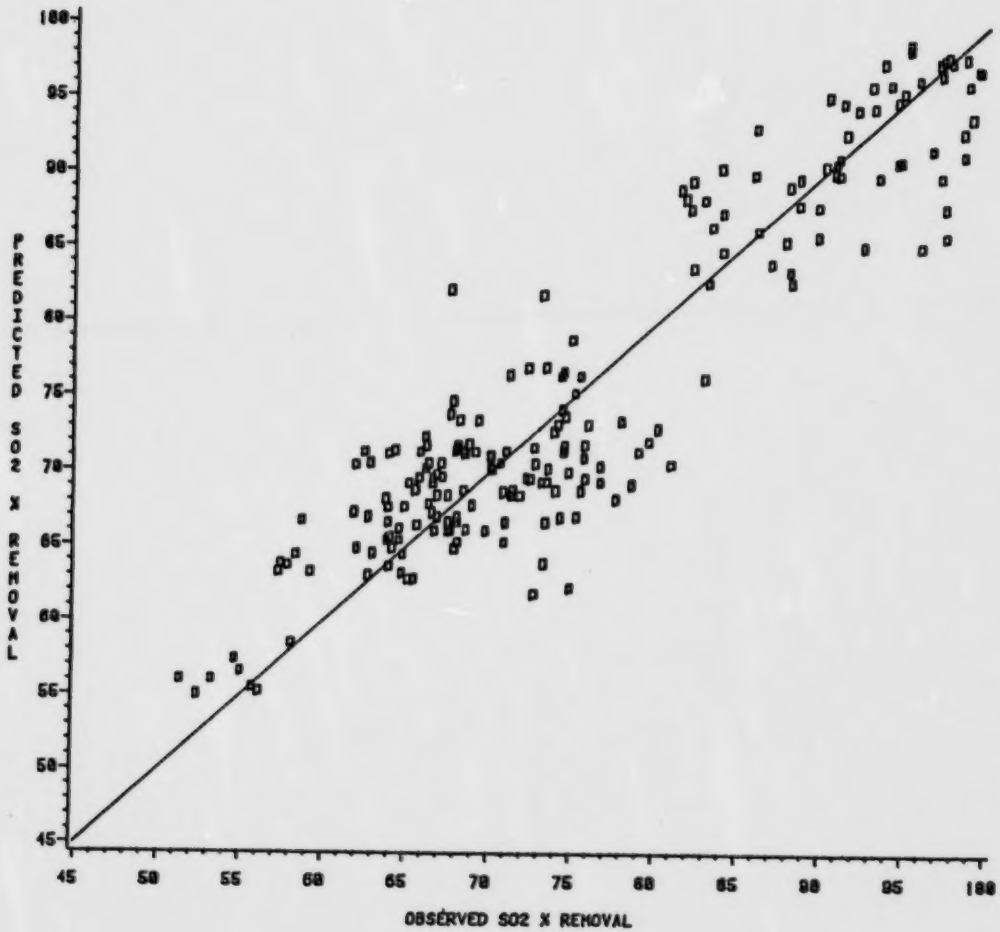


Figure 1-3. Fit of Springfield tray tower data to model.
Removal = 1 - exp[-.00131 Ad - .00216 exp(pH)
- .00996 L/G]

degraded in the system (e.g., oxidation), 4) adipic acid contained in fugitive liquid or slurry losses, and 5) adipic acid that exits with the flue gas. An actual-to-theoretical ratio used to describe adipic acid consumption has been defined in previous studies to be the actual amount of adipic acid fed to the system divided by the amount of adipic acid exiting in the sludge liquor.

Adipic acid consumption data for both natural and forced oxidation operating modes is summarized in Table 1-3. The actual-to-theoretical ratios of approximately 9 for forced oxidation and 5 for natural oxidation are somewhat greater than those observed in the Shawnee prototype testing,[2] but are roughly equivalent to values obtained in bench scale testing under similar conditions.[3] In spite of lower losses of adipic acid in the sludge liquor, higher chemical degradation in the forced oxidation configuration was responsible for the higher actual-to-theoretical ratio observed.

The adipic acid consumption in pounds per ton SO_2 removed is a useful ratio in estimating consumption for proposed systems. During forced oxidation (95 percent SO_2 removal), 9 g/kg SO_2 (18 lbs/ton SO_2) was consumed. The adipic acid consumption for the combined TCA and tray tower modules nearly tripled during natural oxidation testing when the SO_2 removal was increased from 85 (6g/kg SO_2[11 lbs/ton SO_2] to 95 percent (15 g/kg SO_2[29 lbs/ton SO_2]. The consumption rate in forced oxidation tests was less than during natural oxidation testing at 95 percent SO_2 removal as well. This comparison illustrates that the losses in the scrubber liquid were sufficiently reduced by improving dewatering efficiency during forced oxidation to overcome the higher degradation rates.

1.7 OPERATING CHARACTERISTICS

In addition to the significant increase in SO_2 removal capability and the ability to operate at reduced scrubber feed pH to improve limestone utilization, improvements in operating reliability were observed during the demonstration program. FGD system reliability prior to and during the

TABLE 1-3. ADIPIC ACID MATERIAL BALANCE RESULTS

	Forced Oxidation[a] (95% Removal)	Natural Oxidation	
		85% Removal	95% Removal
Adipic Acid Addition (lb/hr)	94	46	113
Adipic Acid Losses in Sludge Liquor (lb/hr)	10	10	21
Actual/Theoretical Ratio[b]	9.4	4.6	5.4
Adipic Acid Consumption (lb/ton SO_2 removed)	18	11	29
Cost (¢/kWh)[c]	0.029	0.017	0.047

[a]During forced oxidation numerous losses of adipic resulted from water discharges in dewatering plant operations. These numbers have been adjusted to reflect more normal operation.

[b]Actual/theoretical ratio = actual adipic acid added/adipic acid lost in sludge liquor

[c]Cost of adipic acid assuming 60¢/lb.

demonstration program is presented in Table 1-4. After the demonstration startup and shakedown period in January and February of 1981, both scrubber modules exceeded an average reliability of 85 percent from March through August. This is a significant improvement in reliability compared to the two previous years. The improvement can be attributed to several factors. First, a number of mechanical improvements were implemented by City Utilities. As a result of the demonstration program, some process operating procedures were revised and additional process engineering input was available. The use of adipic acid also helped improve system reliability by modifying process chemistry so that less scale accumulated on equipment surfaces. While the influence of adipic acid addition on reliability cannot be quantified, some of the operating characteristics attributable to adipic acid are discussed below.

During the forced oxidation period, almost 36 days of continuous operation were logged for both modules. At the end of the testing, only a small amount of solids had accumulated in the TCA cages and mist eliminators. During natural oxidation testing, reliable operation continued although a greater buildup of solids was observed, particularly in the TCA cages. Increased solid accumulation was also observed in the mist eliminators during natural oxidation, but the major cause of the accumulation was probably plugged mist eliminator wash nozzles.

The excellent performance observed during forced oxidation tests is due in part to the relatively high limestone utilization which results in less calcium carbonate dissolution in the absorber. In addition, forced oxidation provided benefical effects such as a larger amount of gypsum seed crystals available as precipitation sites.

The lower pH set point combined with forced oxidation resulted in higher limestone utilization than was observed during the natural oxidation tests. The increase in calcium carbonate and sulfite dissolution during natural

TABLE 1-4. SCRUBBER RELIABILITY[a] DURING ADIPIC ACID DEMONSTRATION PROGRAM

	Module S-1	Module S-2
Average for 1979	34	42
Average for 1980	59	31
1981 Demonstration Program		
Forced Oxidation Tests		
January 10-31	66	85
February	54	35
March	88	81
April	67	97
May	87	66
Natural Oxidation Tests		
June	78	74
July	94	94
August	90	80
Average January 10 - August 31	79	86
Average March 10 - August 31[b]	86	87

[a]Defined as $\frac{\text{hours operated}}{\text{hours required}} \times 100$.

[b]Excludes demonstration startup and shakedown period in January and February.

oxidation can increase the tendency to scale or plug. While an increase in solids accumulation in the TCA module during natural oxidation was observed, the tray module had only a small amount of solids accumulated on the trays and the solids could be removed with a minimum of effort.

It can be concluded that adipic acid addition, while not the sole contributor to improved reliability at SWPP, can allow an FGD system to operate at lower pH and correspondingly higher limestone utilization which should reduce accumlation of solids in the system and improve reliability. Reduced solids accumulation was particularly evident in the forced oxidation testing at SWPP.

Although overall system performance was excellent during most of the program, the air compressor, dewatering equipment, and adipic acid feed system caused operating problems which had to be overcome. Most of these problems can be directly attributable to the temporary retrofit of the system to accommodate the demonstration program and are not reflective of the general use of adipic acid in FGD systems.

A phenomenon that occurred during natural oxidation tests should be considered in systems requiring high SO_2 removals. Limestone blinding (calcium sulfite precipitation on limestone particles) apparently occurred during natural oxidation tests, particularly during testing to achieve 95 percent SO_2 removal. As a result, pH control response was slow. During tests at pH 5.5, the limestone feed could be turned either off or on for 2 hours without a noticeable change in pH. Operation under these conditions can reduce limestone utilization. However, procedures were implemented to reduce the effect of the blinding episodes. Limestone blinding was also observed during forced oxidation tests, but it was caused by air compressor maintenance problems which reduced oxidation efficiency. Sulfite precipitation on the surface of limestone particles can reduce the limestone dissolution rate or reactivity, contributing to reduced limestone utilization.

1.8 DBA TESTING

Approximately one and a half months of testing was conducted to evaluate the performance of dibasic acid (DBA). DBA is a less expensive buffering agent than adipic acid and the feed system for the DBA solution is simpler than the solid handling system required for adipic acid. DBA was tested at 85 percent removal to assess the feasibility of use at SWPP and at 95 percent removal to evaluate its performance under more stringent SO_2 removal requirements. DBA results are summarized in Table 1-5.

The 85 percent removal goal was exceeded in the tray tower at a slightly lower buffer concentration (500 ppm equivalent adipic acid) than required in adipic acid testing (640 ppm adipic acid). However, the average unit load was lower during the DBA tests so the L/G was greater. Lower SO_2 removal was observed in the TCA module, reflecting deterioration due to solids accumulation as observed near the end of adipic acid natural oxidation tests.

A brief test was conducted with DBA to achieve 95 percent SO_2 removal. This goal was achieved in the tray tower at 1300 ppm DBA as adipic acid at a pH of 5.4 compared to 1750 ppm during adipic acid testing. In the TCA module, 94 percent SO_2 removal was achieved at only 1020 ppm DBA as adipic acid, but the gas flow through the TCA module was less than that passing through the tray module.

The concentration of DBA necessary to achieve a given SO_2 removal appeared to be less than adipic acid on an equivalent basis, but the amount of DBA consumed on a weight basis was greater. A feed rate of about 27 kg DBA/hr (60 lb/hr) was required to achieve 85 percent SO_2 removal at 75 percent load factor compared to 20 kg/hr (45 lb/hr) of adipic acid. This translates to about 8g DBA/kg SO_2 (15 lb/ton) compared to 6g/kg SO_2 (11 lb/ton) with adipic acid.

TABLE 1-5. DBA TEST RESULTS

Test Period	Average Scrubber Feed pH	Average DBA Conc. (ppm as Adipic Acid)	Average SO_2 Removal, %
85% SO_2 Removal			
Module S-1 (tray)	5.4	480	90
Module S-2 (TCA)	5.4	420	78
95% SO_2 Removal			
Module S-1 (tray)	5.4	1310	96
Module S-2 (TCA)	5.4	1020	94

The reliability of both modules remained relatively high during the DBA test period. The tray tower operated 98 percent of the time it was required. The TCA module operated with 89 percent reliability. These figures compare favorably with the adipic acid reliability figures.

1.9 SOLID WASTE TESTING

Solid wastes generated during the demonstration program were evaluated for: 1) H_2S generation by fermentation, 2) bioassay results including cytotoxicity, mutagenicity, and acute toxicity, and 3) leachate composition in RCRA and ASTM extraction tests. Four samples were tested to represent the following operating modes: natural oxidation without organic acid addition (baseline), forced and natural oxidation with adipic acid addition, and natural oxidation with DBA addition. The sludge samples were mixed with fly ash collected at SWPP to examine the effects of trace elements in the fly ash. Small quantities of river bank soil (less than 1 percent) were added to the samples to provide a source of bacteria for the fermentation tests.

Fermentation test results indicate that anaerobic decomposition of the solid waste was minimal, both with and without the addition of organic acids. Bioassay results indicate no detectable toxicity or mutagenicity from any of the samples except on the fresh water invertebrate test. In the fresh water invertebrate test, high TDS levels from the solids extracts may be responsible for the toxic effect seen for all of the samples, including the baseline sample without organic acid addition. None of the leachates from any of the sludges exceeded RCRA limits. Likewise, no high values for elements were observed from the ASTM extraction other than those normally associated with FGD systems (calcium, magnesium, sodium, chloride, and sulfate). Therefore, testing of solid wastes from a full-scale organic-acid-enhanced FGD system did not reveal any significant difference from an unenhanced system.

1.10 ECONOMICS

For a savings to be realized from the use of organic additives in limestone FGD systems, the cost of the organic acid and the associated feed system must be offset by reductions in other operating and equipment costs. Improved SO_2 removal capability and more efficient limestone utilization will allow reductions in L/G and limestone stoichiometry. Associated costs for power, limestone, pumps, headers, reagent preparation and solid waste disposal can result.

Based on studies conducted by TVA[4], annual costs can be reduced by about 8 percent by using an adipic-acid-enhanced limestone FGD system in a new 500 MW plant firing high sulfur coal. The amount of savings is influenced by site specific factors such as sulfur and chlorine content of the coal and permit requirements for SO_2 removal. While the incremental cost savings may not be a large percentage, the cost reduction can have a substantial impact on a plant's operating budget.

For existing facilities, the cost reduction that can be realized by using organic acids depends on the specific requirements at that facility and the cost of other alternatives. The types of problems at existing facilities that can be effectively addressed by the use of organic acids include increasing SO_2 removal to meet permit requirements and fuel switching to accommodate higher sulfur coals.

For the case of City Utilities' SWPP, incremental cost estimates for three alternatives to achieve 85 percent SO_2 removal were considered: 1) increasing the L/G in the tray tower, 2) addition of adipic acid, and 3) addition of DBA. The option to increase L/G is a more capital intensive solution because new pumps and headers are required. The adipic acid and DBA options require lower incremental capital costs but higher operating costs.

A present worth analysis of the alternatives was performed using escalation factors consistent with City Utilities' long range planning. The escalation of adipic acid cost ($0.60 per pound in 1981 dollars [$0.32/kg]) and DBA cost ($0.30 per pound in 1981 dollars [$0.66/kg]) closely approximated C.U.'s assumed escalation rate of fuel oil. The escalation cost of electricity (production only) closely approximated C.U.'s assumed escalation rate. The discount factor for the analysis was assumed to be equal to the general inflation rate.

The results of the analysis are illustrated in Figure 1-4. The adipic acid cost option is projected to be less expensive than increasing the L/G during the first 9 years. Beyond that time, L/G modifications are projected to be less expensive. While the adipic acid cost estimates are based on test data at SWPP, the L/G cost estimates are based on past experience with similar systems and greater uncertainty exists in the resulting L/G analysis.

The DBA option is estimated to be less expensive than either of the first two alternatives for the 15 year period used in the analysis. The estimated DBA cost is based on the limited data base provided during the demonstration program. Other options for reducing the cost of DBA that have not been fully investigated might result in a further reduction in cost.

1.11 CONCLUSIONS

The major conclusions concerning the operation of an adipic-acid-enhanced limestone FGD system based upon the results of the demonstration program at SWPP are as follows:

- Adipic acid addition is a feasible method for improving SO_2 removal in systems that are limited by soluble alkalinity in the scrubber slurry feed.

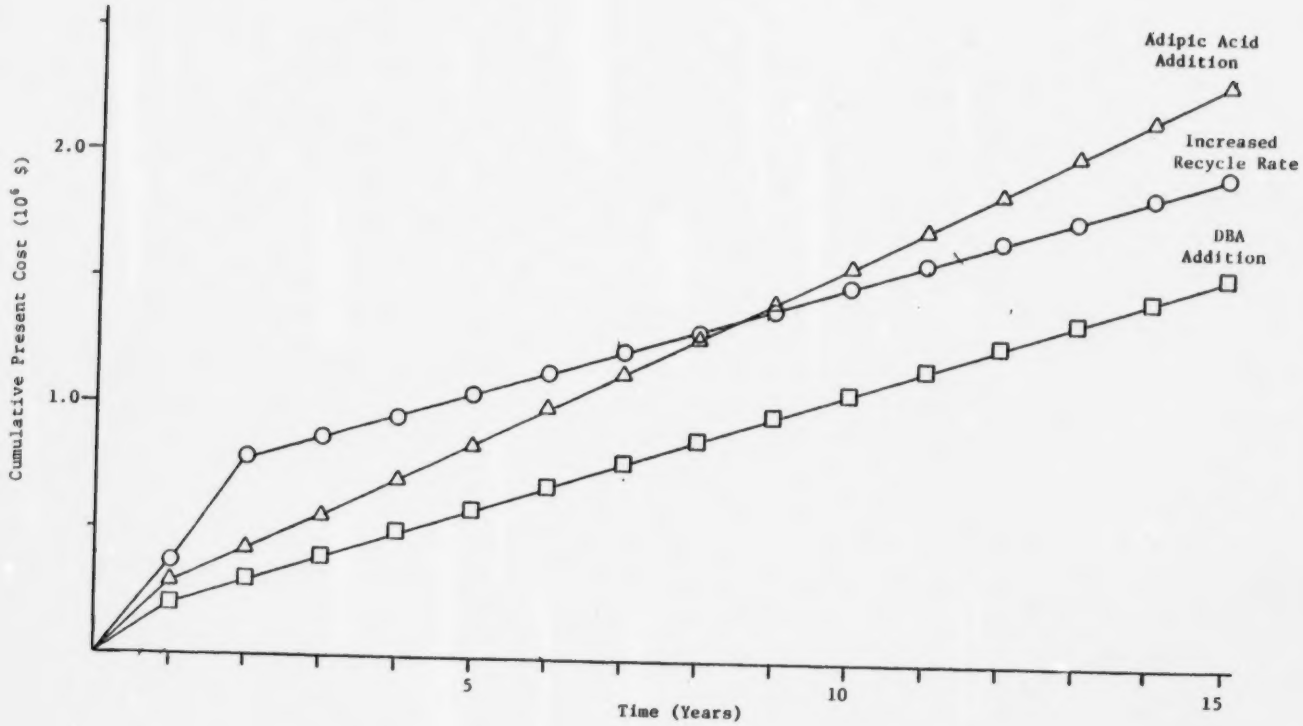


Figure 1-4. Comparison of alternatives for meeting 85% removal at Springifeld.

- The correlations from TCA prototype testing at Shawnee adequately predict full-scale system performance for SO_2 removal as a function of adipic acid concentration and pH;

- Limestone utilization can be improved with adipic acid addition because lower scrubber feed pH is required to achieve a given SO_2 removal.

- Increased limestone utilization from the addition of adipic acid can improve system reliability by reducing the accumulation of precipitating solids, especially in forced oxidized systems.

- The performance of DBA is sufficient to provide an alternative to the use of adipic acid. DBA addition is the least expensive alternative examined for the SWPP to meet requirements for SO_2 removal.

SECTION 2

INTRODUCTION

2.1 BACKGROUND

The majority of FGD systems that are either operating or planned for use in utility applications are lime or limestone based systems. The major driving force for using these "throwaway" systems rather than other FGD technologies is one of economics. Limestone systems are slightly more economical than lime systems because of the cost and energy requirements associated with calcination of the limestone to produce lime[5]. This cost difference is expected to increase with rising energy costs. Although these calcium-based systems are in wide use, their performance (e.g., SO_2 removal efficiency) to date has been limited by reagent reactivity which results in lower soluble alkalinity, relatively higher required liquid-to-gas (L/G) ratios, and larger reaction tanks than other FGD processes.

Organic acids were identified as potentially attractive buffering agents for FGD systems more than 10 years ago[6]. Use of the proper organic acid will buffer the slurry pH in the scrubber and maintain a higher driving force for SO_2 removal. The mechanism is shown by the following reactions using adipic acid as the example organic buffer

$$\text{Sulfur Dioxide + Water} \rightleftharpoons \text{Acidity + Sulfites}$$

$$SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^-$$

$$\text{Adipate ion + Acidity} \rightleftharpoons \text{Adipic Acid}$$

$$\{^-OOC(CH_2)_4COO^-\} + 2H^+ \rightleftharpoons HOOC(CH_2)_4COOH$$

The presence of the organic buffer (adipate ion) reduces the concentration of hydrogen ion, maintains a higher scrubber liquor pH, and improves the SO_2 removal in a system constrained by low alkalinity. The buffering action can also benefit limestone dissolution by maintaining a lower pH in the reaction tank.

Again, using adipic acid as the example, the proposed mechanism is as follows:

Limestone + Water → Hydroxides + Calcium Ion + Carbonates

$$CaCO_3 + H_2O \rightarrow OH^- + Ca^{++} + HCO_3^-$$

Adipic Acid + Alkalinity $\rightleftharpoons$ Adipate Ion + Water

$$HOOC(CH_2)_4COOH + OH^- \rightleftharpoons \{^-OOC(CH_2)_4COO^- + H\ O\}$$

The use of carboxylic acid buffers allows the FGD system to simultaneously achieve good limestone utilization and good SO_2 removal through operation with lower reaction tank pH and higher liquid phase buffering capacity.

Adipic acid was selected for more detailed study based on its buffering region being in the range required for limestone scrubber applications, availability, relatively low cost, nontoxic properties, and solubility in water[7]. Under the sponsorship of EPA's Industrial Environmental Research Laboratory at Research Triangle Park (IERL-RTP), extensive laboratory-, pilot-, and prototype-scale studies on adipic-acid-enhanced limestone systems were conducted. Results of these studies show significant improvement in FGD systems operation over many nonadipic-acid-enhanced limestone systems. These studies indicated that the addition of adipic acid in either conventional or forced oxidation limestone FGD systems should provide the following important benefits:

- Significantly enhanced SO_2 removal efficiencies in either conventional or forced oxidation modes (superior to additives such as MgO which may be of little benefit in forced oxidation systems).

- Increased limestone utilization; hence reduced reagent consumption, decreased waste solids disposal requirements, and more reliable scrubber operation. (These benefits appear to be a result of the ability of adipic acid-enhanced systems to operate at lower pH's while achieving improved SO_2 removal.)

- Lower capital and operating costs than with unenhanced limestone FGD systems.

- Increased system flexibility (e.g., is not adversely affected by chloride); thus, it is especially attractive for closed-loop operation, sulfur variability, load swings, etc.

- Promotes use of less expensive and less energy intensive limestone (rather than lime).

Based on the encouraging results of these initial studies, EPA contracted with Radian Corporation to conduct a full-scale demonstration of adipic acid enhanced system operation at Springfield (MO) City Utilities (C.U.) Southwest Power Plant (SWPP). The Air Correction Division of UOP was subcontracted to make the process modifications required for the demonstration project. The testing began in August 1980, and was completed in October 1981.

2.2 PROGRAM GOALS

The overall objectives of the program were twofold:

- To demonstrate the effectiveness of adipic acid as an enhancement agent for SO_2 removal in a full-scale limestone FGD system.

- To validate the findings from the prototype plant at Shawnee, thereby demonstrating the utility of the Shawnee data base for designing full-scale FGD systems.

To accomplish these objectives, a 6-month field test was planned. Additional field work included 2 months of preliminary testing in the fall of 1980, and 1 month of testing and alternate source of organic buffer (dibasic acid) in September 1981. The test duration was about 9 months and was accomplished in slightly more than a calendar year.

The adipic acid program was divided into 3-month forced oxidation and 3-month natural oxidation test phases. Each phase included 1 month for baseline determinations and 2 months for actual adipic acid testing. The specific goals for both test phases are outlined below:

- To document performance of the system without adipic acid addition (baseline).
- To document conditions required to meet C.U.'s current emission limitation of 1.2 pound $SO_2/10^6$Btu.
- To operate for an extended period achieving:
  - -- 95% SO_2 removal efficiency,
  - -- 95% limestone utilization, and
  - -- 95% sulfite oxidation (during the forced oxidation phase).
- To gather data with instruments certified and operated according to EPA procedures.

At the conclusion of the adipic acid program, a 1-month test was conducted to measure the performance of the system using dibasic acid (DBA) as the buffer. DBA is a mixture of glutaric, adipic, and succinic acids and is a by-product of adipic acid manufacturing. During this month of testing, the additive requirements to achieve emission limits of 1.2 pound $SO_2/10^6$Btu and 95 percent removal were documented.

SECTION 3

FGD SYSTEM DESCRIPTION

The FGD system consists of two parallel Turbulent Contact Absorber (TCA) modules each sized to handle 60 percent of the design flow. (One module was modified to a tray tower in May 1981 before the natural oxidation testing and the other one was modified in October after the completion of the field testing. The conversion to tray towers was in response to repeated plugging and sphere failure with the TCA system.) The coal typically contains from 3.5 to 4.0 percent sulfur, corresponding to inlet flue gas concentrations to the scrubber of 2000 to 2600 ppm SO_2. Typical coal properties are presented in Table 3-1. Limestone preparation, sludge dewatering, and sludge disposal systems are common to the two modules.

Figure 3-1 shows the overall flow scheme for the FGD system. The flue gas enters the presaturator area where it is cooled by clarified liquor (supernatant) from the thickener. The gas then passes through three levels of TCA spheres where SO_2 removal is accomplished, the mist eliminator, and out the stack. No flue gas reheat is used.

Slurry is circulated from the reaction tank below the scrubber through spray nozzles above the top level of spheres (now trays). Makeup limestone is added from the limestone storage tank to the reaction tank to maintain the pH set point. The solids content of the recirculating slurry is controlled by pumping slurry to the thickener. Solids are first settled in the thickener, and the thickener underflow slurry is dewatered on a vacuum filter belt. The resulting sludge is mixed with fly ash in the pug mill and trucked to an on-site landfill. Supernatant (thickener overflow) from the dewatering operation is returned to the FGD modules as presaturator and mist eliminator wash water. Additional supernatant water is utilized in the limestone preparation area.

TABLE 3-1. TYPICAL COAL PROPERTIES FOR C.U.'s SOUTHWEST POWER PLANT

Source: Cherokee Coal (Eastern Kansas)

Analysis Date: March 26, 1980

Ultimate Analysis:

	Weight Percent Dry Basis
Carbon	72.0
Hydrogen	5.1
Nitrogen	1.5
Oxygen	4.8
Sulfur	3.5
Ash	13.1

Proximate Analysis:

	Weight Percent as Received
Moisture	10.6
Volatiles	35.3
Ash	11.7
Fixed Carbon	42.4
Heating Value	11, 796 Btu/lb

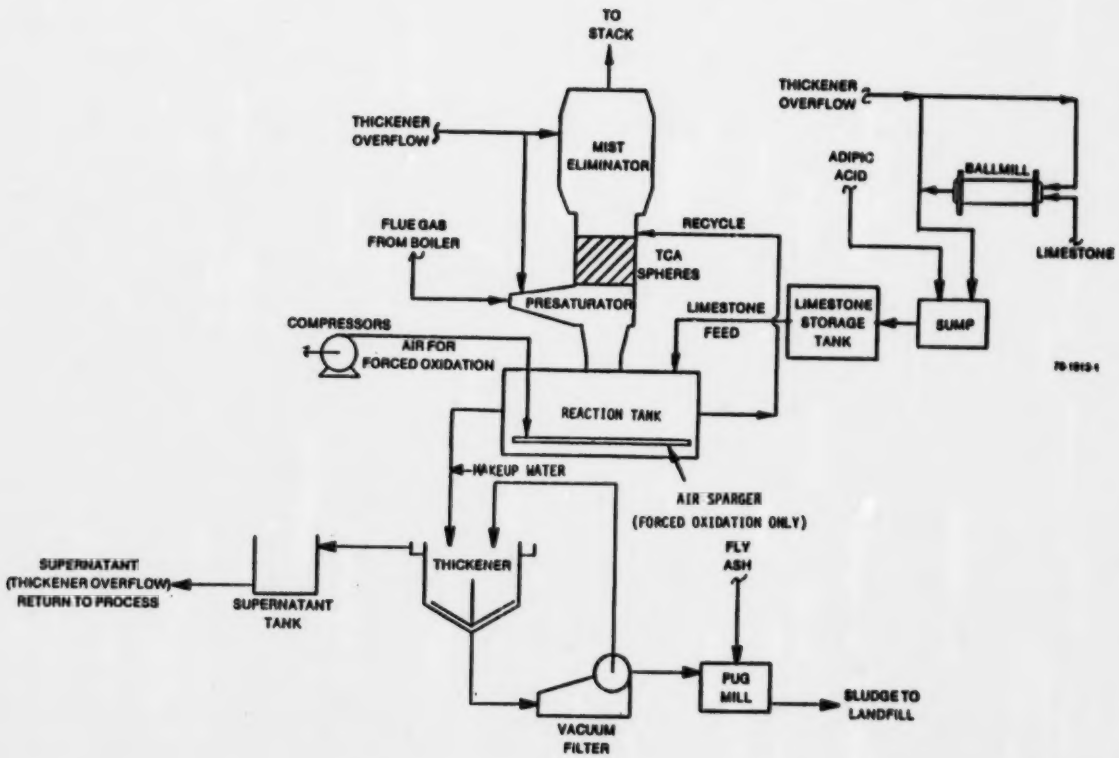


Figure 3-1. Southwest Unit 1 FGD flow scheme.

3.1 LIMESTONE PREPARATION FACILITY

The limestone used in the FGD system is obtained from several quarries around Springfield, and trucked to Southwest Power Plant where it is stored in "ready" piles. Limestone is conveyed from the storage piles to one of two 1500 cubic feet (45 m^3) storage silos prior to being fed to the wet ball mills. Each ball mill is designed to process 9 tons (8160 Kg) of limestone per hour. The resulting slurry is 65 percent solids by weight and 50 to 60 percent through 200 mesh. Plans to upgrade the limestone preparation system to provide 70 percent through 325 mesh are being considered. The slurry from each ball mill is discharged into a 1700 gallon (6440 ℓ) slurry sump. Here, the 65 percent limestone slurry is diluted to a 30 percent solid slurry and pumped to the limestone storage tank. A modification was made to recycle the limestone slurry through the feed system. This modification allows a higher flow rate to be maintained in the limestone feed system, thus reducing plugging problems. Limestone transfer pumps (1 operating/1 standby per scrubber module) feed the limestone slurry to each of the scrubber modules based on an automatic pH control system. Control valves at each of the modules control the amount of limestone makeup fed to the reaction tanks to maintain the pH set point. The remainder of the limestone slurry is recycled back to the limestone storage tank.

3.2 SCRUBBER MODULES

The flue gas stream is split downstream of the electrostatic precipitator and passed through one of the two scrubber modules. Supernatant from the thickener cools the gas entering the presaturation section of the scrubber module from 300 to 125°F (149 to 52°C). The gas then passes through three slurry-contacting stages. Each stage originally consisted of ten 6 ft. x 6.5 ft x 3 ft cages (1.8 x 1.95 x 0.9 m) which contained approximately four inches (10.6cm) of plastic TCA spheres [1.25 inches (3.18 cm) diameter]. In May 1981, the TCA cages in one of the modules were removed and three levels of

perforated trays were installed. The gas flow rate through each module is approximately 300,000 acfm (9000 m^3/min) saturated at 125°F (52°C) at full load conditions.

The scrubber feed slurry is recycled from the 165,000 gal (627 m^3) concrete reaction tank through a 36 inch (91 cm) pipe at a nominal rate of 13,000 gpm (49.4 m^3/min). At full load conditions, the L/G ratio is 40 to 45 gal/1000 acf (6 to 7 ℓ/Nm^3) and the gas phase pressure drop is 10 to 12 inches H_2O (25 to 30 cm). Eighteen spray nozzles are positioned above the top stage of spheres to distribute the slurry. The spent slurry and excess supernatant from the presaturator section drain to the reaction tank. A constant level is maintained in the reaction tanks by gravity overflow to a common sump tank between the two reaction tanks. Slurry is then pumped from the sump to the thickener to control the reaction tank slurry solids concentration at about 10 weight percent.

Before the gas stream leaves the scrubber, it passes through two levels of fiberglass chevron mist eliminators to remove entrained slurry. The lower mist eliminator is continuously rinsed with supernatant water (top and bottom) to prevent solids buildup. Spent wash water is collected in trap out trays below the lower chevrons and drains into the sump between the reaction tanks. The upper mist eliminator is not washed.

The scrubbers are constructed of carbon steel and lined with natural rubber. Reaction tanks are concrete. Duct work connecting both modules to the stack is made of ¼ inch (0.64 cm) carbon steel lined with fiberglass reinforced polyester.

3.3 SOLIDS DEWATERING

Thickener underflow slurry, containing 25 to 40 weight percent solids, is pumped from below the center of the 860,000 gal (3,260 m^3) thickener to the vacuum filter belt. Excess water is removed from the sludge through the

cloth belt by a 15 inch (38.1 cm) H_2O vacuum produced by 300 HP (224 kilowatt) pump. The filtrate is collected in tanks below the belt and then pumped back to the thickener. Overflow from the thickener drains to the supernatant tank where it is pumped to the scrubber modules.

The cake produced from the filtering process contains between 50 and 70 weight percent solids when the system is operating in the natural oxidation mode. This value is dependent upon the oxidation of the sulfite in the reaction tank and the crystal morphology of the solids. At high oxidation levels (forced oxidation) the solids are primarily gypsum and dewater more readily than do calcium sulfite solids. As a final step in the disposal process, the filter cake is mixed with fly ash in a pug mill and trucked to a landfill.

Solids are filtered only when the rake torque exceeds a preset level. When solids are not being filtered, the thickener underflow stream is continuously recycled to the thickener mix well. When necessary, the sludge can be filtered and recylced at the same time to maintain sufficient flow through the underflow lines to avoid plugging.

In case of filtering equipment failure, the thickener underflow slurry can be pumped to either the ash pond or the emergency pond. In this situation, additional makeup water is required by the FGD system to replace the water lost with the slurry.

3.4 ADIPIC FEED SYSTEM

An adipic acid feed system was installed to add adipic acid powder on a continuous basis. Adipic acid is delivered on site in 1100 pound (495 kilogram) sacks. These sacks are loaded by an electric hoist into a two-ton Vibra Screw vibrating silo. The adipic acid is fed from the silo to a Vibra Screw volumetric live bin screw feeder by a Taunton screw conveyor. The adipic acid feed rate from the screw feeder into the limestone sump is set manually. After the adipic acid is mixed with the freshly ground limestone slurry from

the ball mills, the mixture is pumped to the limestone storage tank. Since the limestone handling equipment is common to both scrubber modules, both scrubbers operate with the same adipic acid concentration.

It should be pointed out that the adipic feed system was not designed for long-term use but rather as a temporary structure to be used specifically for this test program. Space limitations imposed by the existing structures in the ball mill building were also fairly severe. Long-term use would dictate a feed system with a larger storage capacity and some type of ground level loading facility. The cost of such a facility was not justified for this short-term project.

3.5 FORCED OXIDATION

Four CENTAC CII-18M2 Ingersoll-Rand compressors were brought on site for the duration of the forced oxidation testing. Each of the compressors was designed to deliver 1800 scfm (54 m^3/min) into a common header which supplied air to the two reaction tanks. The air rate to each reaction tank was calculated stoichiometrically based upon the SO_2 removal in the scrubber and the desired O/SO_2 ratio.

The flow rate from each compressor was regulated by a butterfly valve between the compressor and the common header. Globe valves on the lines from the header to the reaction tanks split the air flow between the two modules. (Globe valve openings were set based on an annubar reading which measured the actual air flow rate to each module).

The air sparge assembly in each reaction tank consisted of 60 one inch (2.54 cm) diameter holes cut in the bottom of six inch (15.2 cm) carbon steel pipe installed in a rectangular configuration. The header was placed three feet (1 m) from each wall of the reaction tank so that the rising air did not place additional stress on the agitator shaft. A more typical design practice would be to place the sparge header in close proximity to the agitator, but

this would have required upgrading the size of the agitator, shaft, gear box, and motor assembly on each reaction hold tank. This expense could not be justified for a three-month demonstration test. However, this design compromise means that agitator horsepower was not utilized to distribute the air, and therefore an optimum forced oxidation system was not demonstrated.

3.6 CONTINUOUS MONITORING

On-line gas analyzers were installed to monitor each scrubber module's performance. Analysis of the flue gas entering each of the two scrubber modules was performed by a DuPont Model 400 SO_2 analyzer modified for two point sampling and a Thermox Model WDG III O_2 analyzer. Likewise, scrubber outlet SO_2 and O_2 concentrations were measured using a DuPont Model 460 and Thermox WDG III analyzer, respectively. This system is described further in Section 4.2.

SECTION 4

DATA ACQUISITION

To adequately demonstrate adipic acid enhanced limestone scrubbing at SWPP, a data acquisition program was developed to achieve the following goals:

1) characterize the performance of the FGD system over a range of operating conditions,

2) identify periods of process upset, and

3) provide routine checks for data quality assurance.

This section describes the overall program developed to satisfy these goals. Section 4.1 discusses the sampling strategy and specific process and chemical data that were monitored to characterize the system. Section 4.2 describes the Continuous Emissions Monitoring System (CEMS) used to measure and record the SO_2 removal efficiency of the two modules. Also presented in this section is a summary of the monitor certification testing results. Section 4.3 discusses the quality assurance work done to monitor and validate the accuracy of both the CEMS and the routine analytical work.

4.1 PROCESS CHARACTERIZATION

A sampling strategy was developed to investigate the effect of the major SWPP scrubber operating variables on the traditional parameters used to characterize or measure the performance of limestone scrubbers. The FGD performance variables for which data were routinely gathered included:

- SO_2 removal efficiency,
- limestone utilization,
- sulfite oxidation,
- scaling potential, and
- reliability.

Scrubber operating variables were monitored routinely to document their effect on the performance of the FGD system. Monitoring these operating variables not only helped describe the performance of the SWPP scrubbers but also gathered information which was needed to compare their performance to that of the Shawnee prototype scrubber. In addition, data were gathered to identify periods of process malfunction or upsets.

Table 4-1 through 4-3 present the gas, liquid, solid and slurry sampling and data gathering frequency used to characterize the FGD system. The analytical techniques employed are summarized in Appendices A and B. Table 4-4 lists the process data that were recorded hourly by the scrubber operator. Independent checks of process data were made by the Radian shift engineer.

In this program, SO_2 removal efficiency was the most important variable used in measuring the performance of the scrubbers. Monitors were installed so that the removal efficiency of each module could be measured separately. Section 4.2 describes in detail the Continuous Emissions Monitoring System used to track SO_2 removal.

Limestone utilization is another important FGD system performance variable. Limestone utilization is defined as the moles of SO_2 absorbed divided by the moles of limestone ($CaCO_3$) added to a scrubber. Since the limestone feed stream flows intermittently, and because of the errors associated with measuring the slurry and gas flow rates the most reliable method of determining limestone utilization is from a solids analyses as shown in Equation 4-1.

TABLE 4-1. GAS PHASE DATA FREQUENCY OF MEASUREMENTS PER WEEK

Species	Module S-1		Module S-2	
	Flue Gas In	Flue Gas Out	Flue Gas In	Flue Gas Out
SO_2	Continuous	Continuous[a]	Continuous	Continuous[a]
O_2	Continuous	Continuous[a]	Continuous	Continuous[a]
H_2O	--	1	1	1

[a]Outlet SO_2 and O_2 concentrations were manually measured once every two weeks (one scrubber sample each week) to verify continuous readings. Other quality assurance measures for the continuous monitoring system are described later in this section.

TABLE 4-2. LIQUID PHASE DATA FREQUENCY OF MEASUREMENTS PER WEEK

Species	Module S-1		Module S-2		Thickener Overflow	FGD System Make-up Water	
	Scrubber Feed	Scrubber Bottoms	Scrubber Feed	Scrubber Bottoms		Well Water	Cooling Tower Blowdown
Ca	1	1	1	1	½	¼	¼
Mg	-	1	-	1	-	¼	¼
Na	-	1	-	1	-	¼	¼
SO_3	1	1	1	1	½	¼	¼
SO_4	1	1	1	1	½	¼	¼
Cl	-	1	-	1	-	¼	¼
NO_3	-	½	-	½	-	¼	¼
Adipic Acid	7	-	7	-	7	-	-
Buffer Capacity[a]	7	-	7	-	7	-	-

[a]Buffer capacity analyses done during DBA test phase.

TABLE 4-3. SLURRY AND SOLID PHASE DATA FREQUENCY OF MEASUREMENTS PER WEEK

Species	Module S-1		Module S-2		Limestone Slurry	Thickener Underflow	Filter Cake
	Scrubber Feed	Scrubber Bottoms	Scrubber Feed	Scrubber Bottoms			
Slurry							
Temp	7	1	7	1	-	-	-
pH	7	1	7	1	-	-	-
Wt% Solids	14	-	14	-	5	5	5
Solid Phase							
Ca	1	-	1	-	½	-	½
Mg	1	-	1	-	½	-	½
SO_3	1	-	1	-	-	-	½
SO_4	1	-	1	-	-	-	½
Inerts	1	-	1	-	½	-	½

TABLE 4-4. HOURLY PROCESS DATA

SOUTHWEST POWER STATION

Date _____

	12 MN	1 AM	2 AM	3 AM	4 AM	5 AM	6 AM	7 AM	8 AM	9 AM	10 AM	11 AM	12 N	1 PM	2 PM	3 PM	4 PM	5 PM	6 PM	7 PM	8 PM	9 PM	10 PM	11 PM	12 MN	Avg
A and B Scrubbers																										
Unit Load (MW)																										
Inlet Flue Gas Temp (°F)																										
Ball Mill Feeder Speed																										
B-1																										
B-2																										
Precip. Outlet Press. (in. H_2O vac)																										
A - Scrubber																										
Demister Diff. (in. H_2O)																										
Scrubber Diff. (in. H_2O)																										
Slurry Recycle																										
Pump #																										
Amps																										
Discharge Press.																										
Hold Tank																										
pH																										
Density																										
Draw Off Flow (gpm)																										
% SO_2 Removal																										
Presat. Outlet Temp. (°F)																										
"A" ID Fan Amps																										
"A" ID Fan Outlet Press. (in. H_2O)																										
Limestone Makeup Valve Position (% of scale)																										
B - Scrubber																										
Demister Diff. (in. H_2O)																										
Scrubber Diff. (in. H_2O)																										
Slurry Recycle																										
Pump #																										
Amps																										
Discharge Press.																										
Hold Tank																										
pH																										
Density																										
Draw Off Flow (gpm)																										
% SO_2 Removal																										
Presat. Outlet Temp. (°F)																										
"B" ID Fan Amps																										
"B" ID Fan Outlet Press. (in. H_2O)																										
Limestone Makeup Valve Position (% of scale)																										

12-8 Operator _____
Shift Supervisor _____

8-4 Operator _____
Shift Supervisor _____

4-12 Operator _____
Shift Supervisor _____

$$\text{Limestone Utilization} = \frac{M_s}{M_{Ca\ solid}} \qquad (4\text{-}1)$$

where M_s = the moles of total sulfur per gram of solids, and

M_{Ca} = the moles of calcium per gram of solids.

Limestone utilization data reveals several important factors for evaluating the performance of a scrubber. First, the lower the utilization, the larger the requirement for limestone for a given level of SO_2 removal. Low limestone utilization increases capital, operating and maintenance charges associated with the limestone preparation facility. The presence of excess limestone for systems operating with low utilizations (below about 80 percent) may cause scaling problems in the tower due to either the quantity of limestone dissolving in the contactor, or to secondary SO_2 scrubbing on the mist eliminators. In addition, disposal costs of the FGD sludge will increase since the quantity of excess limestone will result in larger volumes of waste.

Sulfite oxidation is defined as the moles of calcium sulfate divided by the moles of calcium sulfite plus calcium sulfate in the solid phase as shown in Equation 4-2:

$$\text{Sulfite Oxidation, \%} = \frac{\text{Moles } CaSO_4}{\text{Moles } CaSO_4 + \text{Moles } CaSO_3} \times 100 \qquad (4\text{-}2)$$

With the system operating in the natural oxidation mode, sulfite oxidation is not a controlled variable, but is influenced by site specific equipment design such as L/G ratios and by various operating set points such as scrubber feed pH. The sulfite oxidation rate is an important parameter to monitor since lower sulfite oxidation rates cause higher loss rates of adipic acid. This relationship occurs because adipic acid selectively coprecipitates or becomes occulded in the sulfite crystals (but does not coprecipitate to a great extent in the sulfate crystals). For a forced oxidized system, sulfite oxidation is the measure of the oxidation equipment performance. Sulfite oxidation data can be used to optimize the oxidation air rate so that only the minimum air

required (and therefore, minimum compressor power) is used to achieve a target oxidation level.

The scaling potential of a scrubber is another important operating characteristic of the system. It is typically evaluated by measuring liquid phase concentrations of ionic species in the scrubbing slurry. Analytical results were input to the Radian Species Distribution Model where relative saturations for scaling species were calculated (see Section 5.3.4). The relative saturation is an indication of the tendency of the slurry to deposit chemical scale on equipment. Gypsum scaling, the most troublesome scaling problem in limestone systems, is usually initiated when the relative saturation is above about 1.3. The relative saturation was monitored to document changes in scaling potential caused by adipic acid addition.

The plan for the demonstration testing was to operate for relatively long periods of time at only a few sets of operating conditions to document the fluctuations which can typically occur during full-scale commercial operation. In addition, testing at a relatively constant condition for a period of several months can help evaluate the longer-term reliability of the system. Although a several-month test cannot answer all questions, any trends discovered can be useful and maintenance-prone equipment can be identified. Long-term effects concerning materials of construction cannot be fully evaluated in a one-year test however.

Information on the performance of the limestone preparation and sludge dewatering facilities was also collected to provide a more complete characterization of the FGD system. Although the data collected in this area were not as extensive as that gathered from scrubber operations, sufficient information was recorded to evaluate the subsystems as they impacted the overall performance of the FGD system.

4.2 CONTINUOUS EMISSIONS MONITORING SYSTEMS

The Continuous Emissions Monitoring System was designed to provide SO_2 removal data consistent with the requirements of an FGD demonstration program. To satisfy these requirements, the system had to be capable of gathering data which: 1) would show the effect of changing FGD system variables on SO_2 removal efficiency, and 2) would be consistent with EPA regulations for gathering continuous emissions data.

Construction of the Southwest Power plant was completed in 1978, making it subject to the 1971 EPA New Source Performance Standards (NSPS) for utility boilers[8]. This standard required that no more than 1.2 pounds of SO_2 be emitted per million Btu thermal heat input to the boiler. Compliance with this standard requires monitoring only the exit flue gas in the power plant stack (since the standard is not based on a percent SO_2 removal, inlet and outlet scrubber concentrations need not be measured). The 1979 revision to the utility boiler NSPS also includes the SO_2 emission ceiling of 1.2 lbs $SO_2/10^6$ Btu[9]. In addition, it mandates a percentage reduction of SO_2 emissions determined from a sliding scale based upon the sulfur content of the coal burned. Compliance with this standard, therefore, requires monitoring the flue gas into and out of the FGD system on a continuous schedule. To meet EPA requirements for data capture, at least two data points must be taken each hour for a minimum of 18 hours per day. The goal for the continuous emissions monitoring system is to collect at least 4 data points per hour for all 24 hours.

Since the 1979 utility standard is the most recent one, the monitoring system was designed to record SO_2 emission information necessary for determining compliance with the percent removal regulations. Collecting compliance data for both inlet and outlet scrubber concentrations provided the necessary documentation for determining the effect of FGD operating variables on SO_2 removal.

4.2.1 Continuous Monitoring Equipment

The monitoring system operates by periodic extraction of a sample of flue gas from the plant duct work and analysis of the gas for its SO_2 and O_2 concentrations. Analysis of the flue gas entering each of the two scrubber modules is handled by a DuPont Model 400 SO_2 analyzer modified for two point sampling and a Thermox Model WDG III O_2 analyzer. For analysis of the flue gas exiting each scrubber, a DuPont Model 460 and Thermox WDG III analyzer arrangement similar to that at the scrubber inlet is used.

Figure 4-1 shows the location of the instruments and sample ports with respect to the scrubber. The locations of the sample ports were limited to those installed during construction of the plant. They represent the best locations for determining the individual performance of the two modules.

Each of the four sample acquisition systems consist of:

1) a 30 micron stainless steel mesh filter and shield,

2) a 1/2 inch (1.27 cm) stainless steel probe fixed in the center sample port,

3) fifty feet of 400°F (204°C) self-limiting, heat traced, insulated, 1/4 inch (0.6 cm), double tube, Teflon sample line, and

4) a moisture trap located in the DuPont analyzer.

At each sample location, the filter is positioned in the centroid of the duct. The centroid is defined as the innermost one percent crossectional area of the duct. This location was selected as part of the procedure outlined in the EPA Continuous Emissions Monitoring Certification Test[10]. Results of the monitoring system certification are discussed in the next section.

To monitor the performance of both modules, the analyzers cycle from one scrubber to the other every six minutes. The inlet and outlet of one

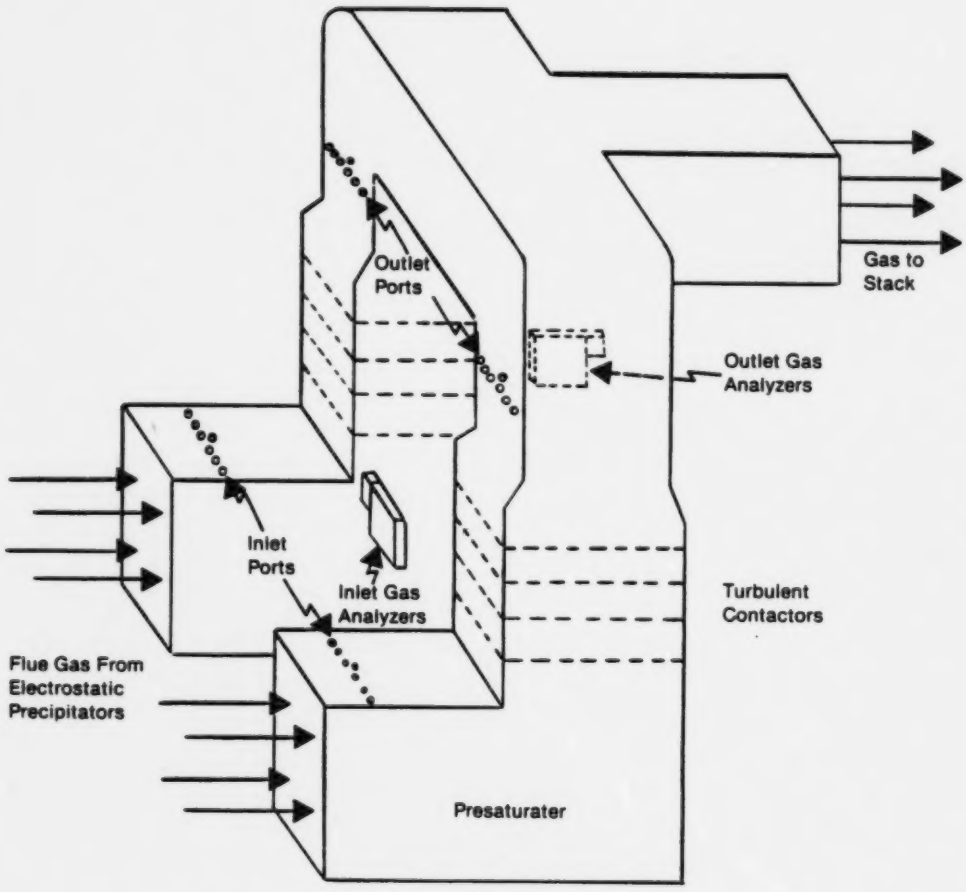


Figure 4-1. Location of Continuous Monitors and Sample Ports.

module are sampled simultaneously for three minutes of the six minute period. For the other three minutes, regulated instrument air purges the instruments and sample acquisition lines to reduce problems with corrosion and pluggage.

The signal outputs from the analyzers are recorded by two separate data acquisition systems. Primary data logging is accomplished using a Radian Dart II microprocessor. A six-point chart recorder serves as backup to the microprocessor to maximize data capture. Table 4-5 is an example of the hourly report furnished by the microprocessor. In addition, at the end of a day, a daily report is printed which includes all the hourly averages and a 24 hour average. The SO_2 and O_2 values measured by the analyzers are used to compute CO_2 emissions into and out of the scrubbers on a pounds per million Btu boiler heat input basis. The emission numbers are calculated using the EPA developed dry F-factor calculation. Mositure values for the flue gas before and after the scrubbers are measured manually on a routine basis. These numbers are averaged and input to the microprocessor for its use in calculating SO_2 emissions. The gas samples were kept above the moisture dewpoint to prevent water condensation in the sample acquisition system lines. The continuous monitoring data for the entire program are presented in Volume II.

4.2.2 Certification of Continuous Emissions Monitoring System

Following installation of the analyzers, sample acquisition system, and data recorders, the entire monitoring system was tested according to the "Proposed Rules" published in the Federal Register (Vol. 44, No. 197) for certification of a continuous emissions monitoring system.

The operational test lasted from January 25 through March 1, 1981. During this time, the SO_2 monitoring system operated a minimum of 168 hours. Although the continuous monitoring system was available to operate for all but 6 hours of this period, it did not gather data continuously throughout the certification testing period due to FGD system failures. The certification testing schedule is illustrated in Figure 4-2 along with the scrubber availability for this period.

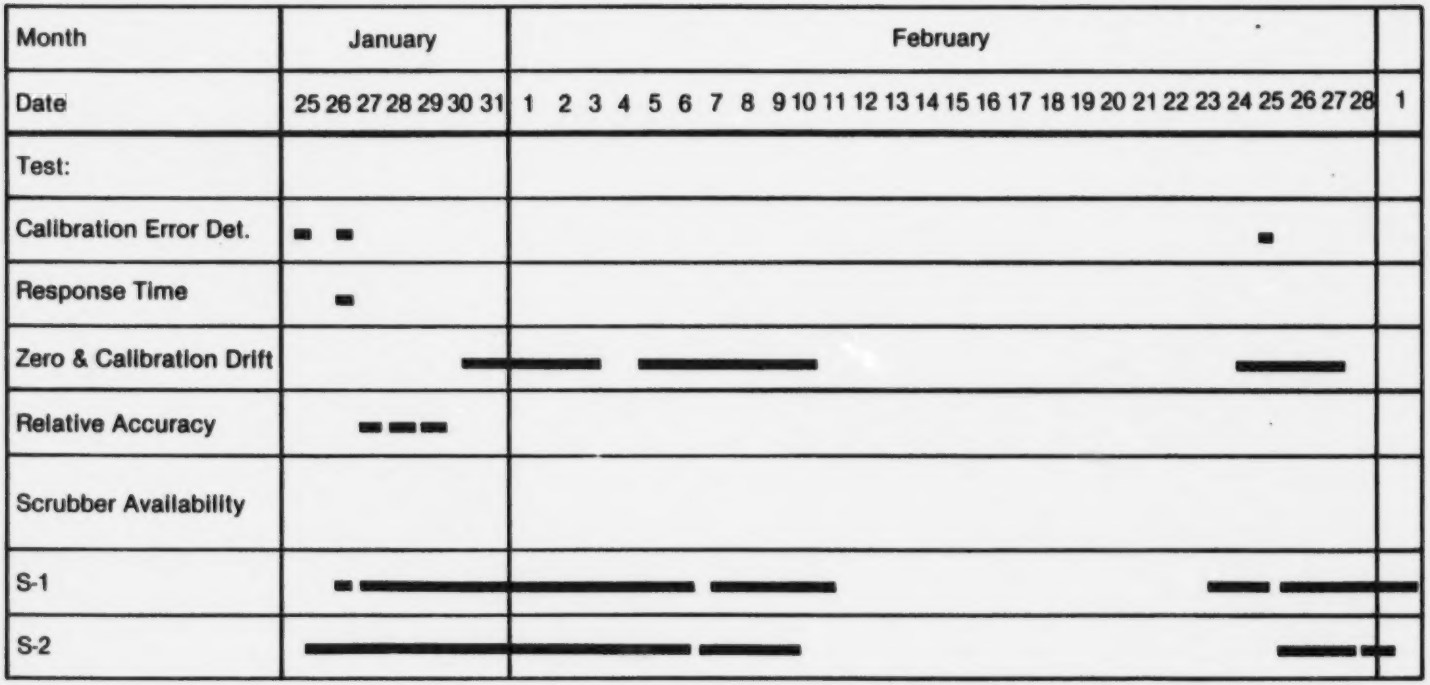


Figure 4-2. Certification testing schedule.
Southwest Power Plant - Springfield, MO

TABLE 4-5. DART HOURLY REPORT FORMAT

ADIPIC ACID DEMO

** CHANNEL HOURLY REPORT **
HOUR = 08
REPORTED AT 09:00:00 24 AUG 1981

LABEL	OBSERVATIONS									
	08:01:05	08:07:05	08:13:05	08:19:05	08:25:05	08:31:05	08:37:05	08:43:05	08:49:05	08:55:05
S1 INLET SO2		2091.92		2138.31		2195.06		2113.77		2136.85
S1 OUTLET SO2		82.31		86.28		77.44		54.99		93.99
S1 INLET O2		6.74		6.53		6.37		6.62		6.48
S1 OUTLET O2		6.21		5.99		5.82		6.08		5.92
INLET H2O	0.080	0.080	0.080	0.080	0.080	0.080	0.080	0.080	0.080	0.080
OUTLET H2O	0.140	0.140	0.140	0.140	0.140	0.140	0.140	0.140	0.140	0.140
S1 IN LB/MMBTU		5.81		5.84		5.92		5.82		5.82
S1 OUT LB/MMBT		0.24		0.25		0.22		0.16		0.22
S1 % SO2 RED		95.82		95.72		96.27		97.24		95.35
S2 INLET SO2	2089.37		2127.48		2125.48		2173.00		2141.37	
S2 OUTLET SO2	65.37		64.11		69.66		62.72		57.84	
S2 INLET O2	6.76		6.50		6.50		6.23		6.29	
S2 OUTLET O2	5.84		5.77		5.69		5.65		5.72	
S2 IN LB/MMBTU	5.82		5.80		5.79		5.80		5.75	
S2 OUT LB/MMBT	0.19		0.18		0.20		0.18		0.17	
S2 % SO2 RED	96.79		96.86		96.60		96.95		97.05	

LABEL	AVERAGE
S1 INLET SO2	2135.18
S1 OUTLET SO2	79.00
S1 INLET O2	6.55
S1 OUTLET O2	6.01
INLET H2O	0.08
OUTLET H2O	0.14
S1 IN LB/MMBTU	5.84
S1 OUT LB/MMBT	0.23
S1 % SO2 RED	96.09
S2 INLET SO2	2131.74
S2 OUTLET SO2	64.34
S2 INLET O2	6.46
S2 OUTLET O2	5.74
S2 IN LB/MMBTU	5.79
S2 OUT LB/MMBT	0.18
S2 % SO2 RED	96.85

Table 4-6 summarizes the results of the certification tests. In each case, the SO_2 continuous monitoring system at Southwest Power Plant met the required specification listed in the Federal Register. The calibration error is higher for the mid-level gas than for the high-level gas. While the difference is insignificant in this case, a minor linearity problem in the analyzers and/or recorders might exist. The response times were all well below the required 15 minutes. The only value that was close to the specification was the 24-hour calibration drift on the outlet DuPont. A daily zero and subsequent span adjustments on the anlayzers kept them within the specified drift values.

The only monitoring system equipment failure occurred February 3. Tubing pluggage in the inlet Thermox interrupted a 24-hour Zero and Calibration Drift Test. The tubing was replaced and the inlet O_2 24-hour drift test series was repeated. The monitoring system was out of service for about 6 hours.

For more detail concerning the certification testing, refer to "Results of Certification Testing at Springfield City Utilities Southwest Power Plant," presented in Volume II.

4.3 QUALITY ASSURANCE PROGRAM

A quality assurance program was developed for the Adipic Acid Demonstration Program to ensure the accuracy of the data generated. The program was designed to monitor data from three primary sources:

- the routine laboratory analytical work,
- the Continuous Emissions Monitoring System, and
- the process instrumentation.

Each source of data required a unique quality assurance effort. This section describes the quality assurance work for each.

TABLE 4-6. SUMMARY OF CERTIFICATION TESTING AT CITY UTILITIES SOUTHWEST POWER PLANT, SPRINGFIELD, MISSOURI

Test	Results					Specification
Calibration Error Determination		Calibration Error (%)				
		Mid-level gas		High-level gas		
	Analyzer	DART	Chart	DART	Chart	≤5% of each mid-level and high level calibration value
	Inlet DuPont	2.6	3.0	1.8	1.6	
	Inlet Thermox	3.8	2.0	1.9	1.3	
	Outlet DuPont	1.6	0.4	1.6	0.9	
	Outlet Thermox	2.6	2.1	1.9	1.4	

Response Time	Location of Gas Introduction	Gas Used	Response Time (Min)	Specification
	S-1 Inlet	SO_2	2.17 downscale	≤15 minutes
		O_2	2.02 same	
	S-2 Inlet	SO_2	2.00 upscale	
		O_2	1.60 upscale	
	S-1 Outlet	SO_2	3.46 upscale	
		O_2	3.19 upscale	
	S-2 Outlet	SO_2	1.45 downscale	
		O_2	2.25 downscale	

Zero and Calibration Drift		Zero Drift (% of span)				Calibration Drift (% of span)				Specification
		DART		Recorder		DART		Recorder		
		2-hr	24-hr	2-hr	24-hr	2-hr	24-hr	2-hr	24-hr	
	Inlet SO_2	0.29	0.52	0.22	0.63	0.42	1.49	0.32	1.20	≤2% of span value for 2 hr ≤2.5% of span value for 24 hr
	Inlet O_2	0.06	0.12	0.08	0.25	0.35	1.95	0.25	1.50	
	Outlet SO_2	0.85	0.82	0.76	1.17	1.00	2.35	1.16	2.30	
	Outlet O_2	0.06	0.35	0.04	0.15	0.93	0.80	-[1]	0.80	

Relative Accuracy (% difference)		DART	Recorder	Specification
	Inlet	4.71	4.97	≤20% of the mean reference method test data, in terms of emission factors
	Outlet	9.62	10.36	

[1] 2-hour calibration test for chart recorder not completed. Successful completion of the same test performed on the DART was ruled sufficient.

4.3.1 Quality Assurance (QA) for Analytical Data

The QA program for routine analytical work was based on procedures and recommendations described in two sources:

- "EPA Handbook for Analytical Quality Control in Water and Wastewater Laboratories," (EPA-600/4-79-019)[11], and
- "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans," QAMS-005/80, (Office of Monitoring Systems and Quality Assurance, Office of Research and Development, United States Environmental Protection Agency)[12].

A complete description of QA practices and procedures used for the program is presented in Appendix A of this report. This section will present a brief summary of the QA program.

There are two distinct areas which were addressed in the development of the QA program. The first is the various practices and procedures utilized in the technical work performed to ensure reliable data. The second distinct QA area addresses verification and documentation of the technical data generated.

Specific QA practices and procedures were employed for all aspects of the analytical protocol. These aspects included: sampling of the various liquid, solid and gas phase streams, analysis of the collected samples, data reduction, data flow and data reporting, and maintenance and performing verification of the various instruments and equipment used.

Quality control procedures employed to verify the accuracy and reliability of the technical work performed included:

- analysis of quality control standards,
- replicate analysis of quality control samples,
- analysis of samples in duplicate,

- analysis of spikes,
- analysis of calibration standards and blanks, and
- performance of laboratory audits.

The QC data generated for the program are documented and presented in Appendix A. Included are Shewhart charts, which are used to summarize and evaluate results of the QC standards and samples analyzed by plotting their percent recovery. Also presented in the Appendix A are mean percent recoveries and standard deviations for QC samples and standards for the various parameters analyzed.

4.3.2 Quality Assurance for Continuous Emissions Monitoring Data

An important objective of the Demonstration Program was to install and operate monitoring equipment on the two SWPP scrubber modules which compiled with the specifications set forth by EPA in the October, 1979 Federal Register[13]. During a scheduled scrubber outage which lasted from October to December, 1980, a system was designed and installed as described in Section 4.2. Certification of the system following its installation provided a thorough check of the accuracy and precision of the output from the monitors. The monitoring system passed each of the tests in the certification procedure as shown in Section 4.2.2.

To maintain a close check on the accuracy of the monitors on a day to day basis, a quality assurance plan was developed based on procedures and recommendations contained in the Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods[14]. The plan consisted of three routine checks:

1) mid-point span and zero,
2) Method 6 runs, and
3) SO_2 stratification traverses.

The mid-point span and zero checks were made daily to control span and zero drift. Results were recorded and used to identify equipment manfunctions and leaks. The experience gained over the course of the test program indicated that daily checks were not necessary for controlling instrument drift. However, the daily checks were important in early identification of instrument performance/manfunction. Results of the span and zero checks are presented in Volume II.

The relative accuracy of the monitors was tested on a weekly basis. An EPA Method 6 triplicate run was performed each week to provide another check on the performance of the monitoring system. The sample for the relative accuracy test was drawn through the same probe used by the continuous monitor. This was necessary because of the degree of stratification of SO_2 at the location where the flue gas exiting such scrubber was measured. At times, even differences of 6 inches (15 cm) in probe location resulted in significant differences in measured SO_2 concentrations. The results of the Method 6 relative accuracy tests done over the course of the test program are presented in Volume II.

Stratification traverses were performed periodically to document the difference between the SO_2 concentration at the duct centroid where the continuous monitors extract the gas sample for analysis and the bulk gas phase SO_2 concentrations in the duct at various other locations along that cross-section of the duct. The first traverses were performed as part of the certification work. They showed that there was little or no stratification of SO_2 concentration in the flue gas at the location where the scrubber inlet gas was measured. There was significant SO_2 stratification in the flue gas at the location where the scrubber outlet gas was measured. However, the SO_2 concentration at the centroid was within 10 percent of the bulk gas concentration for each of the four traverses made during certification testing. Following the addition of adipic acid, however, this percentage difference increased. While the absolute differences did not increase, the percentage difference did increase due to the lower SO_2 concentrations present with the

adipic acid. Problems with recycle nozzle pluggage and maldistribution of the TCA spheres were common and may have contributed to greater stratification of SO_2. Stratification traverses were made periodically on the two scrubber outlet ducts throughout the program to document the difference between the reported and actual SO_2 concentrations. Volume II presents the results of each of these traverses.

4.3.3 Quality Assurance for Process Instrumentation Readings

The City Utilities operations staff was responsible for recording certain control room instrumentation information for the program. Several of these readings were very important and monitoring and evaluating their accuracy was the objective of a daily effort. The Radian shift engineer checked and recorded the reaction tank pH and ID fans amps among other readings at least twice a shift. Manual measurements of the pH values were made at least twice a day by Radian. In addition, the City Utilities plant chemist calibrated each pH instrument daily.

SECTION 5

FORCED OXIDATION TEST PHASE

The SWPP scrubber train was designed and constructed as a natural oxidation system. In October and November, 1980, the scrubbers were modified for forced oxidation testing. The modifications to the FGD system were relatively simple, involving only the installation of an air sparge assembly in each reaction tank and an air delivery system consisting of air compressors and headers. Because the testing was for only a three-month period, expensive modifications such as the installation of a more powerful agitator in each tank and upgrading the design and operation of the dewatering plant to handle the calcium sulfate sludge were not justified. The objective of this project was to demonstrate the effectiveness of adipic acid in a full-scale forced oxidation system, not to demonstrate an optimized forced oxidation design. Section 5.1 describes the equipment installed for the testing, Section 5.2 describes the test plan, and Section 5.3 discusses the results. Appendix C contains a detailed data summary for the forced oxidation test program.

5.1 FORCED OXIDATION EQUIPMENT

Four CENTAC CII-18M2 Ingersoll-Rand air compressors were used to provide the air for forced oxidization. Each compressor was capable of delivering 1800 scfm (54 m^3/min). The air flow to each module could be controlled independently through a series of valves. The total of 7200 scfm (190 Nm^3/min) allowed oxidation at stoichiometries of greater than 3 lb-atoms of oxygen per lb-mole of SO_2 absorbed at boiler full load conditions for each module.

The air sparger consisted of a six inch (15.2 cm) carbon steel pipe installed near the walls and about 2 1/2 feet (0.75 m) off the bottom of each

reaction tank. Air entered the tank through one-inch (2.5 cm) diameter holes in the bottom of the sparger. Normal liquid height in the reaction tanks was about 20 feet (6 m) resulting in 17.5 feet (5.25 m) of air/slurry contact height. The sparger was placed near the tank walls so that the rising air did not place significant stress on the agitator shaft. More typical design practice would be to place the sparge header directly beneath the agitator. However, this would have required expensive upgrading of the agitator assembly on each reaction tank to handle the additional shear stress. The design compromise meant that agitator horsepower was not utilized to distribute the air so an optimum forced oxidation system was not demonstrated. The less efficient oxidizer could have exacerbated sulfite blinding of the limestone as discussed in Section 5.3.4. However, the demonstration of an optimum forced oxidation system was not of paramount importance since forced oxidation had already been demonstrated on a commercial scale[15].

5.2 FORCED OXIDATION TEST PLAN

The forced oxidation test phase was originally scheduled to be conducted over a three-month period. It was to consist of one month of baseline testing followed by two months of adipic acid testing. Table 5-1 shows the test conditions planned for the forced oxidation testing. The major operating variables tested included scrubber feed pH, adipic acid concentration, and oxygen-to-SO_2 ratio. The effect of the TCA spheres on SO_2 removal efficiency was also tested at the request of City Utilities.

The objective of the baseline test phase was to characterize the performance of the SWPP FGD system without adipic acid. The results from this work are used to determine the magnitude of the effect adipic acid addition has on system performance, controllability, and ease of operation.

Module S-1 was tested without TCA spheres over the baseline period. This testing was conducted to gather data on the performance of the towers without the failure prone spheres. Module S-2 was tested with the normal height of

FIGURE 5-1. FORCED OXIDATION TEST PLAN

	Test Conditions			
	Level of TCA Spheres, in	Scrubber Feed pH	Adipic Acid Concentration (ppm)	Air/SO_2 Ratio (Atoms O/Moles SO_2 removed)
Baseline (one month duration)				
Module S-1	0	5.5	0	as required for 95% sulfite oxidation
Module S-1	12	5.2	0	
Module S-2	12	5.5	0	
Adipic Acid Testing (two months duration)				
Module S-1	0	5.4	(1)	as required for 95% oxidation
Module S-1	12	5.0	(2)	
Module S-2	12	5.0	(2)	

[1]as required for 85 percent SO_2 removal

[2]as required for 95 percent SO_2 removal

approximately four inches (10 cm) of spheres in each of its three levels. The air rate for 95 percent sulfite oxidation was determined. Two pH set points were established so that the maximum amount of steady-state data could be attained. The pH's tested were the 5.5 set point, typically used by SWPP, and 5.2 which approached the recommended pH for adipic acid testing based on the Shawnee test results. The baseline testing extended from January 10, 1981 through February 10, 1981.

Following the one-month baseline test period, a two-month adipic acid test was planned (February 10 to April 23, 1981). There were several important objectives established by EPA for the adipic acid/forced oxidation test phase. These included:

- Operating the system for 30 or more days at 95 percent SO_2 removal, 90 percent limestone utilization, and 95 percent sulfite oxidation with minimum limestone blinding.
- Document operating conditions required to meet the 1.2 lbs $SO_2/10^6$Btu in the module without the TCA spheres.
- Gather SO_2 removal data with monitors that had been certified according to EPA procedures.

The first test conducted was a one-week test of Module S-1 without TCA spheres. The purpose of this test was to determine if the scrubber could comply with the Federal SO_2 regulation at SWPP using adipic acid without the troublesome TCA spheres. After about one week of testing with adipic acid, the spheres were placed back into the scrubber and it was returned to normal operation.

Because one of the program objectives was to verify Shawnee results at full-scale operation with normal performance fluctuations, the remainder of the testing was essentially at one set of conditions. The initial test conditions were identified as optimum operating points based on runs at Shawnee (which simulated the Springfield FGD system). The initial control set points were modified as necessary to achieve the stated test objectives mentioned above.

5.3 FORCED OXIDATION TEST RESULTS

This section presents the results of the forced oxidation test phase. The performance of the scrubbers is compared with and without aidpic acid addition, and SO_2 removal efficiency results are also compared to those predicted by the Shawnee data base. The section is organized according to the following key operating variables:

- SO_2 removal efficiency
- Limestone utilization
- Sulfite oxidation
- Sulfite blinding
- Scaling potential
- Adipic acid consumption

5.3.1 SO_2 Removal Efficiency

Figures 5-1 and 5-2 show the time-phase relationship between adipic acid concentration and SO_2 removal efficiency for Modules S-1 and S-2, respectively. The dramatic effect that adipic acid concentration had on the SO_2 removal efficiency between the baseline and adipic acid testing is readily evident from these figures. General improvements in SO_2 removal were made during adipic acid testing as more experience was gained in minimizing the episodes of sulfite blinding and undesired liquor discharges. Better control techniques led to decreased occurrences of liquor discharge and blinding beginning in late March after the initial process shakedown. During the April 15 to April 23 period, only Module S-2 operated and liquor laden with adipic acid was again frequently purged from the system causing system performance to suffer slightly.

Table 5-2 summarizes the SO_2 removal results for the forced oxidation testing. During baseline testing, with no adipic acid in the system, Module S-1 had an average SO_2 removal efficiency of 46 percent at a pH set point of

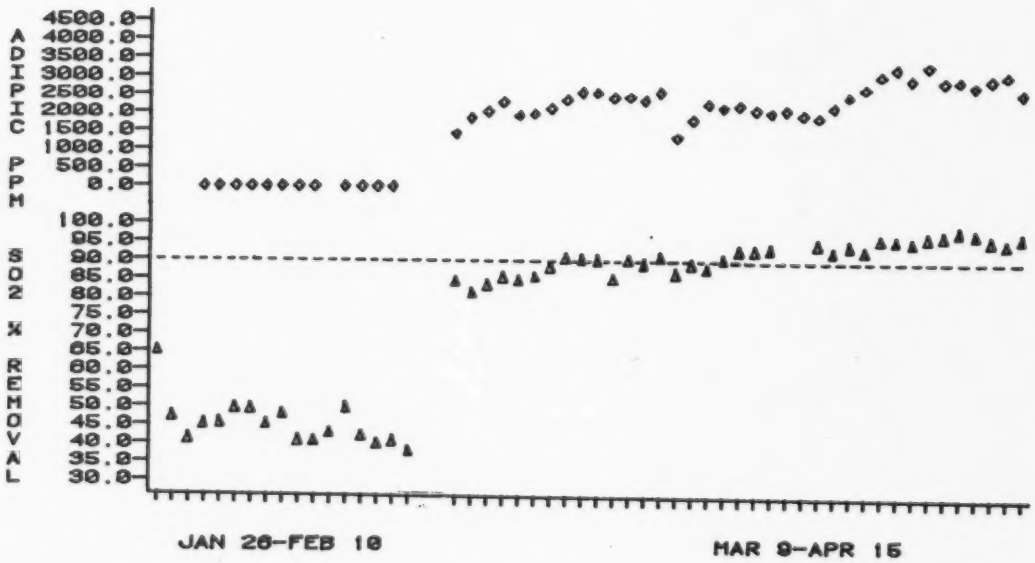


Figure 5-1. Summary of SO_2 removal for forced oxidation/adipic acid testing in Module S-1.

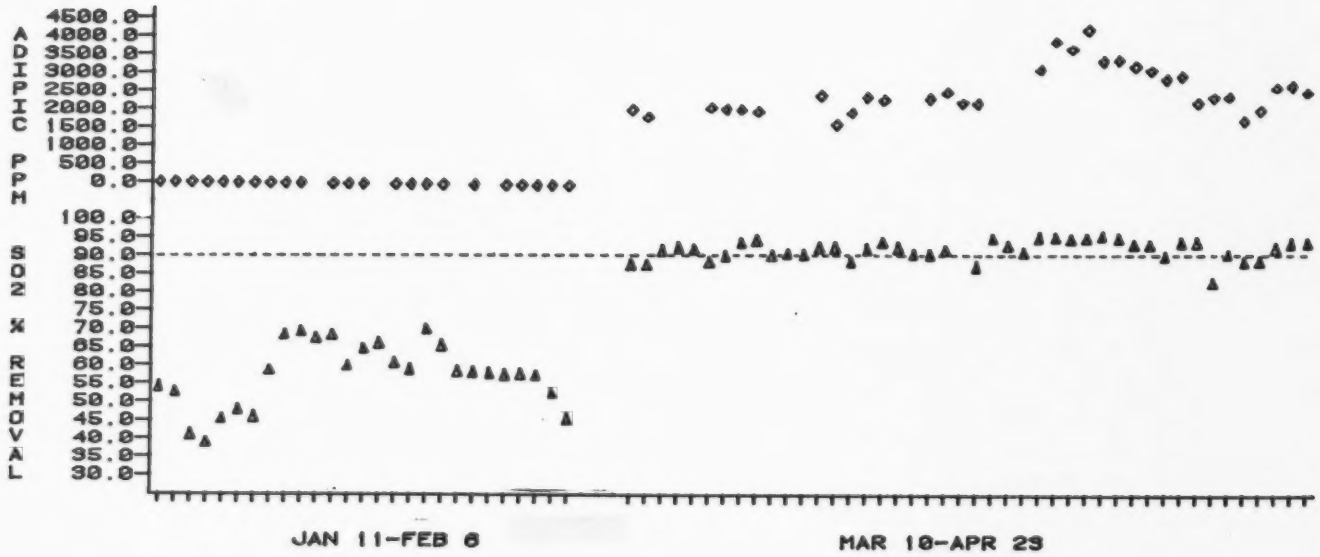


Figure 5-2. Summary of SO_2 removal for forced oxidation/adipic acid testing in Module S-2.

TABLE 5-2. SUMMARY OF SO_2 REMOVAL DURING FORCED OXIDATION TESTING

	Operating Time (Hours)	pH	Adipic Acid (ppm)	Atoms O/ Mole SO_2 Removed	SO_2 Removal (%)
Testing Without TCA Spheres (Module S-1)					
Baseline (Jan. 10-Feb. 10, 1981)	468	5.4	0	3.1	46
Adipic Acid Addition (Feb. 10-March 1)	135	5.4	1340	2.8	84
Testing with TCA Spheres					
Baseline - Module S-2 (Jan. 10-Feb. 10)	579	5.4	0	3.0	58
Adipic Acid Addition[a]- Module S-2 (Feb. 10-April 23)	1168 (312)	5.0 (5.0)	2410 (3323)	3.0 (3.2)	91 (96)
Adipic Acid Addition[a]- Module S-1 (March 1-April 15)	960 (312)	5.1 (5.3)	2340 (3000)	1.3 (1.0)[b]	89 (95)

[a] Average results are presented in this table. The results in parenthesis represent performance after startup and shakedown problems had been resolved.

[b] Reduced air rate due to poor air compressor availability and oxidation in Module S-1 was sacrificed to avoid sulfite blinding problems (see Section 5.3.4).

5.5 (overall average of 58 percent at pH 5.4). The significant difference between the performance of the two modules at pH 5.5 is attributed to S-1 being operated without TCA spheres.

Beginning February 23 and extending thorugh March 1, S-1 was tested with adipic acid without the TCA spheres. Over the seven day test period, the SO_2 removal efficiency averaged about 84 percent. Adipic acid concentrations in the reaction tank were varied from 900 ppm to 2800 ppm and pH values were varied from 5.4 to 5.8. Figure 5-3 presents the results of this testing. As was expected, relatively high concentrations of adipic acid were required to achieve the 85 percent SO_2 removal "compliance" level because of poor gas-liquid contacting. The results indicate that at pH 5.5 from 1500 to 2200 ppm adipic acid would be required to maintain the unit in compliance. Eighty-five percent was chosen as the compliance removal level since SWPP is subject to the 1971 emission standard of 1.2 lbs $SO_2/10^6$Btu. Depending on the coal sulfur level, the SO_2 removal efficiency required to keep emissions below this level was usually 82 to 83 percent. The 85 percent level, therefore, would give a conservative but safe set point. The results also showed that at pH 5.7 and adipic acid concentrations above 2500 ppm, the module operated at better than 90 percent SO_2 removal. The TCA spheres were replaced in Module S-1 on March 2 and 3.

Adipic acid testing with TCA spheres in Module S-1 began on March and continued through April 15, 1981. Testing with adipic acid in Module S-2 began February 10. Module S-2 operated with TCA spheres throughout the entire adipic acid forced oxidation test period. Table 5-2 shows the SO_2 removal efficiency of Module S-1 with TCA spheres averaged 89 percent over the adipic acid test period. The removal efficiency of Module S-2 averaged 91 percent during adipic acid testing.

As seen in Table 5-2, the target SO_2 removal level of 95 percent was not obtained during adipic acid testing. There are several reasons why the 95 percent target was not reached, including early forced outages, initial process

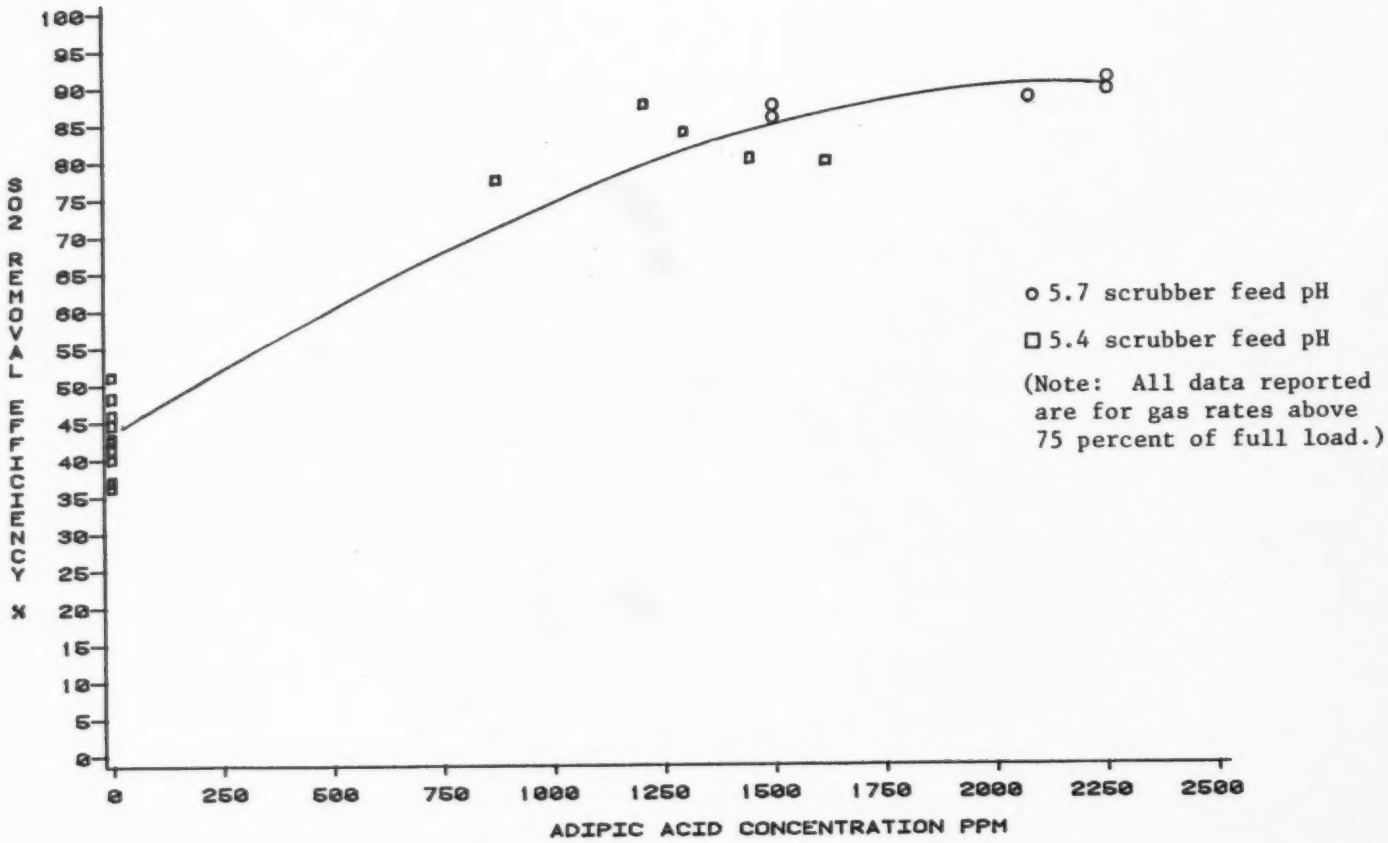


Figure 5-3. Results of testing without TCA spheres.

control problems, and SWPP module performance that was slightly lower than predicted from the Shawnee data.

From February 10 to March 13, the FGD system experienced several forced outages which made system control and performance sporadic. (See Section 8.0 for system reliability during the program.) From March 13 to April 15, Module S-1 operated nearly 100 percent of the time and Module S-2 operated essentially full-time from March 13 to April 23. Table 5-3 presents the distribution of days that each module operated within a given range of removal efficiency over these periods. The table as well as Figures 5-1 and 5-2 show the improvement in controlling the modules' SO_2 removal efficiency at 95 percent from April until the end of the forced oxidation testing. This improvement reflects the experience gained in operating the system during February and March. Specifically, control of fugitive water losses and control of sulfite blinding episodes (Section 5.3) were responsible for improved process performance.

TABLE 5-3. DAYS OF OPERATION AT INDICATED SO_2 REMOVAL EFFICIENCY

Module (Date)	85-90%	90-95%	95+%
S-1			
(3/13-4/15)	9	15	8
(4/1-4/15)		7	8
S-2			
(3/13-4/23)	3	21	16
(4/1-4/23)	3	8	14

Another reason for the slightly lower SO_2 removal efficiency experienced early in the adipic acid test period was that the TCA modules' performances were slightly lower than expected from Shawnee results. The SO_2 removal efficiencies measured at SWPP were compared with the following SO_2 removal correlation developed from the Shawnee results[16].

$$\text{Fraction } SO_2 \text{ Removal} = 1 - \exp\{-0.0047 \exp(pH + 0.00062\ Ad)\} \qquad (5\text{-}1)$$

where Ad represents the adipic acid concentration of the scrubbing liquor (ppm) and pH is the pH value of the scrubber feed slurry. The Shawnee correlation predicts slightly higher removal efficiencies than were routinely achieved at Springfield. Using the same general form as the Bechtel model, a correlation was developed which gave the best fit to the Springfield data. The modified correlation for Springfield is:

$$\text{Fraction } SO_2 \text{ Removal} = 1 = \exp\{-0.0042 \exp(pH + 0.00065\ Ad)\} \qquad (5\text{-}2)$$

Figure 5-4 shows both the prediction from Equation 5-2 and the acutal results from the Springfield test program. The figure shows that the TCA's at SWPP averaged from 2 to 5 percent lower SO_2 removal than predicted from the Shawnee correlation.

The differences between the Shawnee predictions and SWPP observations could be attributed to a number of reasons, all of which would result in reduced gas-liquid contacting efficiencies. First, the total height of TCA spheres in the Shawnee scrubber was 15 inches (38 cm) compared to 10 to 12 inches (25.4 to 30.5 cm) in each module at SWPP. This reduced the surface area over which SO_2 scrubbing could occur. Both the gas and slurry flow rates (on an equivalent cross-sectional area basis) were lower at Shawnee. In addition, approximately 30 percent of the 30 sphere cages in each of the modules were found empty at the end of the testing at SWPP. The access doors to these cages had slipped open allowing the spheres to migrate to adjacent cages. A check of the condition of the nozzles through which the slurry is fed to each of the towers showed 3 plugged completely and 4 partially plugged out of the 18 nozzles present in Module S-1. Module S-2 and 2 nozzles plugged completely and 4 partially plugged. Another reason for lower SO_2 removals than predicted from the Shawnee correlation could be differences in the limestone grind. The limestone grind at SWPP (60 percent less than 200 mesh) was substantially

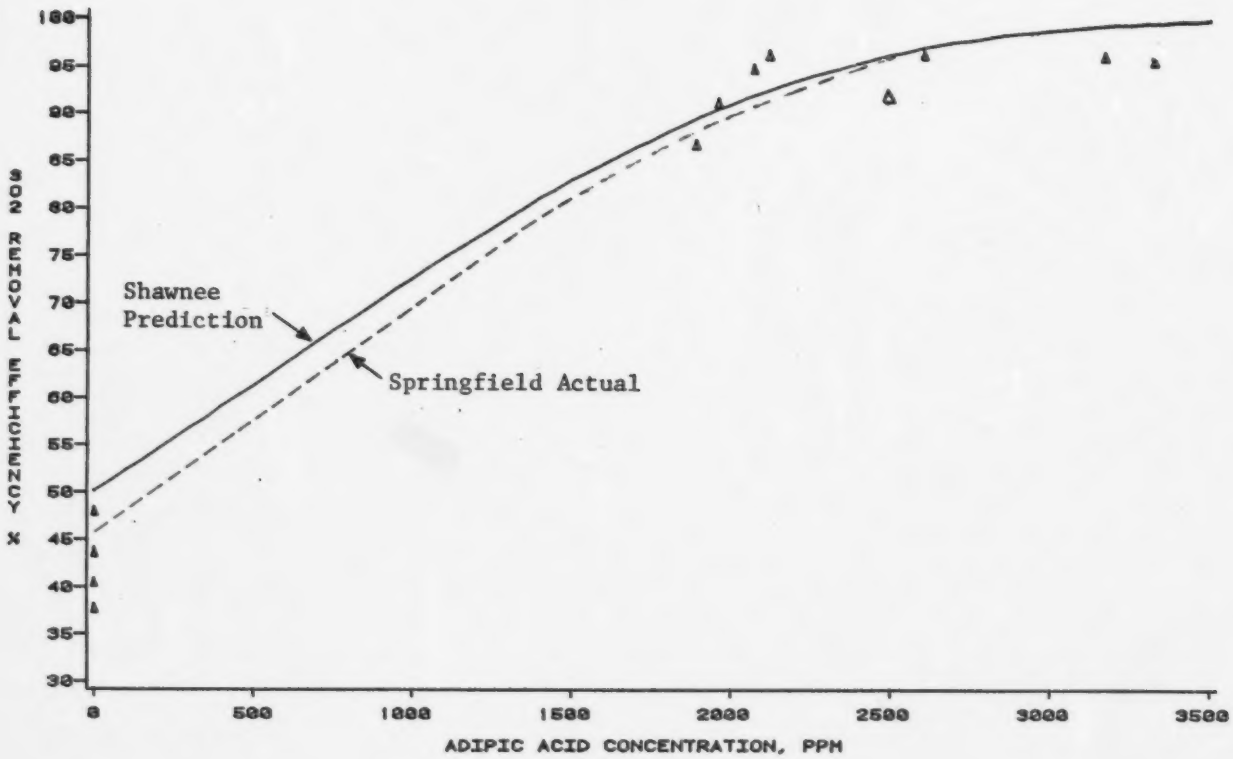


Figure 5-4. Fit of Springfield data to Shawnee Predictive Model, scrubber feed pH 5.0.

coarser than that normally used at Shawnee (90 percent less than 325 mesh). These problems would result in reduced gas-liquid contacting efficiency in the towers and could account for the lower observed removals.

Increases in adipic acid concentrations during the program emphasized the gas-slurry contact limitations. For example, an adipic acid concentration change from 2250 ppm to 3000 ppm resulted in an increase from 90 to 95 percent SO_2 removal in Module S-2 at a pH of 5.0. Increases in adipic acid concentration above 3000 ppm showed relatively little increase in SO_2 removal. The SO_2 removal should not be liquor alkalinity limited at above 3000 ppm adipic acid concentration, and the relatively constant removal noted with increasing adipic acid concentration is indicative of physical gas-liquid contact limitations.

The results also indicated a noticeable difference between the performance of the two modules. S-1 typically showed about two percent lower SO_2 removal efficiency than did S-2. Some of the possible causes include: (1) the liquid feed flow was slightly lower in S-1 due to the condition of the recycle pumps and pipe arrangement differences on that module, (2) the gas flow was consistently higher through S-1 because of mechanical problems with the S-2 fan, and (3) the oxidation efficiency was routinely lower in S-1 than in S-2 because of compressor malfunctions. While variations in the L/G ratio and oxidation efficiency with each module's data set did not appear to be statistically significant with respect to SO_2 removal efficiency, the operating differences noted above could have caused the differences in SO_2 removal efficiency between the two modules.

Overall, the Shawnee correlation predicted the SWPP results fairly close. These correlations should be quite useful in process design activities.

5.3.2 Limestone Utilization

Limestone utilization is a measure of how efficiently a limestone FGD system makes use of its calcium carbonate reagent. The majority of the calcium carbonate reacts with absorbed SO_2 forming either calcium sulfite or sulfate. In many limestone FGD systems, good reagent limestone utilization is not achieved while meeting SO_2 emission regulations, and poor utilization contributes to a number of problems. Use of adipic acid as a buffer permits both good SO_2 removal and limestone utilization to be attained simultaneously. Excess limestone reagent increases raw material cost and sludge disposal requirements and may lead to scaling or plugging problems. Table 5-4 presents the results of the utilization measurements made over the baseline and adipic acid test periods.

TABLE 5-4. LIMESTONE UTILIZATION DURING FORCED OXIDATION TESTING

Test Period	Average Scrubber Feed pH	Limestone[a] Utilization	Limestone[b] Stoichiometry
Baseline			
Module S-1 (without spheres)	5.4	89	1.12
Module S-2	5.4	88	1.14
Adipic Enhanced			
Module S-1 (without spheres)	5.4	89	1.12
Module S-1 (with spheres)	5.1	91	1.10
Module S-2	5.0	92	1.09

[a]Solid phase moles sulfur to calcium ratio (M_s/M_{ca} x 100)

[b]Moles of limestone added to scrubber divided by the moles of SO_2 absorbed.

During both baseline and the adipic acid testing, limestone utilizations typically remained above 85 percent. The values shown in Table 5-4 for adipic acid testing exclude periods when sulfite blinding occurred. Sulfite blinding

which affects limestone dissolution, is discussed in detail in Section 5.3.4. If data taken during the blinding periods are considered, the average limestone utilization for S-1 drops from about 90 percent to about 85 percent while for S-2 it remains about 90 percent. This difference may be due to the fact that higher oxidation air rates were used in S-2 which helped that module recover from sulfite blinding much more quickly than S-1. The normal operating procedure of sacrificing oxidation in S-1, when the compressors malfunctioned, limited the available air rate therefore making this module more vulnerable to sulfite blinding.

The major conclusion which can be drawn from the limestone utilization data is that 90 percent utilization can be achieved simultaneously with high SO_2 removal efficiency if adipic acid is used as a buffer. Baseline tests showed close to 90 percent limestone utilizations, but system design limitations prevented good SO_2 removal from being attained. Good limestone utilization remained even when greater SO_2 removal was achieved with adipic acid. In other applications where improvement in SO_2 removal is not the primary concern, it is anticipated that limestone utilization could be improved by the addition of adipic acid since the system could be operated at a lower pH without a decrease in SO_2 removal.

5.3.3 Sulfite Oxidation

Table 5-5 presents the average sulfite oxidations measured during the baseline and adipic acid test periods. The two primary variables which affected sulfite oxidation were the reaction tank pH and oxidation air rate or O/SO_2 ratio (atoms oxygen/mole SO_2 absorbed). Generally, this system required in excess of a 3 to 1 ratio to achieve full oxidation even at 5.0 pH. A more typical requirement for 95 percent oxidation with a well designed forced oxidation system is 2 atoms oxygen for each mole of SO_2 absorbed. As stated previously, the important finding in this program is that adipic acid functioned well in a commercial scale forced oxidation system. The actual performance of the forced oxidation system was only important in that limitations led to episodes where sulfite blinding occurred which adversely affected SO_2 removal and limestone utilization.

TABLE 5-5. SULFITE OXIDATION DURING FORCED OXIDATION TESTING

Test Period	pH	O/SO_2 Ratio	Sulfite Oxidation
Baseline			
Module S-1 (Without spheres)	5.4	3.1	95
Module S-2	5.4	3.0	91
Adipic Enhanced			
Module S-1 (Without spheres)	5.4	2.8	90
Module S-1 (With spheres)	5.1	1.3	74
Module S-2	5.0	3.0	94

Malfunction of the air compressors and problems with sulfite blinding required that S-1 Module be partially oxidized (about 75 percent oxidation) during the aidpic acid testing. Module S-2 was kept fully oxidized as long as two or more compressors were available for operation. Since all four compressors were required to fully oxidize (greater than 99 percent oxidation) both modules and since oxidation efficiencies of 90 to 95 percent led to frequent episodes of sulfite blinding, it was felt that the most reliable method of operating the scrubbers was to provide full oxidation of S-2 (99+ percent) and partial oxidation of S-1.

The handling properties of the dewatered solids improved significantly during the forced oxidation testing. The solids content of the filter cake averaged about 80 percent over this test phase as opposed to the more normal value of between 50 and 60 percent solids for the filter cake during natural oxidation. The forced oxidized solids were more stable and did not rewet like the calcium sulfite solids typically do. The faster settling sulfate solids did cause some operating problems in the dewatering facility which resulted in discharges of liquor containing adipic acid. These operating problems are discussed in Section 8 while the effect of these problems on adipic acid material balances are discussed in Section 5.3.5.

5.3.4 Sulfite Blinding

Sulfite blinding is a phenomenon in which high levels of dissolved sulfite apparently react with calcium dissolving from limestone particles to form a calcium sulfite coating on the limestone surface. This coating restricts further limestone dissolution. As a buffer, adipic acid increases the SO_2 removal per volume of scrubber slurry, thereby increasing the dissolved sulfite concentration. If the oxidation efficiency is not sufficiently high, the sulfite precipitates on the limestone particle effectively inhibiting limestone dissolution. This phenomenon seems to be enhanced in forced oxidation by the relatively low amount of calcium sulfite seed crystals available for sulfite desupersaturation in the slurry. The results of limestone blinding are a drop in the reaction tank pH, an increase in the limestone makeup rate, and a decrease in limestone utilization.

Limestone blinding was not a complete surprise at SWPP since it had been observed at Shawnee. There were two principal causes of blinding at SWPP: (1) increases in boiler load without accompanying increases in oxidation air; and (2) air compressor failure. The boiler load increase early in the morning caused the greatest number of blinding episodes. At the beginning of the program the air rates were adjusted to optimize the O/SO_2 ratio. However, the early morning load change was made by City Utilities generally prior to 6 AM without immediate readjustments of the air rates. This seemed to initate the blinding problems. Eventually, instead of optimizing the air rate to each scrubber, the air rate was left at full capacity in S-2 to avoid the blinding in that module. Chronic problems with the compressors limited oxidation in Module S-1.

The initial objective had been to achieve 95 percent oxidation in each module. However, this level of oxidation did not sufficiently lower the liquid phase sulfite concentration nor did it provide sufficient solid phase calcium sulfite for precipitation seed crystals. Thus, limestone blinding occurred which resulted in lowered pH values, SO_2 removal efficiencies, and limestone

utilization. Either oxidation rates much less than 90 percent or in excess of 99 percent were found to minimize problems. The 90 to 95 percent oxidation was determined to be the worst point for blinding.

Two mechanisms were found to escape blinding once it occurred. One was to increase the air rate up to O/SO_2 ratios of about 4, which in effect, oxidized the sulfite on the limestone surface and alleviated blinding. This was the usual approach taken with Module S-2. The second approach was to only partially oxidize the sulfite leaving sufficient calcium sulfite crystals for sulfite precipitation. Module S-1 was generally operated at below 85 percent oxidation once it became evident that the 4 compressors could not reliably supply air at a 3.0 O/SO_2 ratio. The second approach to eliminating blinding took much longer than increasing the O/SO_2 ratio. Typically 2 to 4 hours of partial oxidation were required before normal pH control was resumed, whereas increasing the O/SO_2 ratio regained pH control in less than 30 minutes. Partial blinding, resulting in sluggish pH control and increased limestone consumption, was also noted and occurred at times for lengthy periods before corrections were made. Unless the pH and SO_2 removal dropped suddenly as in severe blinding cases, the reason for increased limestone flow was not determined immediately.

5.3.5 Chemical Scaling

The formation of calcium sulfate (gypsum) scale in limestone scrubbers can be a serious problem if the scale growth rate is high. Generally, the precipitation of gypsum occurs through orderly crystal growth mechanisms on existing sulfate solids. However, when the dissolved concentrations of calcium and sulfate reach high levels, normal precipitation may not be able to desupersaturate the calcium and sulfate before nucleation occurs and the formation of small gypsum particles may occur. Rapid precipitation, caused by high calcium and sulfate concentrations, and nucleation, usually marks the onset of gypsum scaling on the tower internals.

To document the effect of adipic acid addition on the scaling potential of the slurry, major and minor ionic species were routinely measured in the slurry fed to the towers and in the slurry as it exits the lower contacting stage of each tower. The measured concentrations were input to the Radian Species Distribution Model to predict the calcium sulfate relative saturation. Relative saturation is defined as:

$$R.S. = \frac{(a_{Ca^{++}})(a_{SO_4^{=}})(a_{H_2O})^2}{K_{sp}} \qquad (5\text{-}3)$$

where R.S. = relative saturation of gypsum,

$a_{Ca^{++}}$ = activity of free calcium in the liquid phase

$a_{SO_2^{=}}$ = activity of free sulfate in the liquid phase, and

K_{sp} = solubility product constant for $CaSO_2 \cdot 2H_2O$.

Table 5-6 presents the results of the model for the Baseline and Adipic Acid Test periods. Past observations have shown that gypsum scaling typically occurs at relative saturations above 1.3 or 1.4[17]. As Table 5-6 shows, both modules operated below this level for both the baseline and adipic acid test periods. No major scaling was observed in either of the absorber towers, as predicted by the model results. Section 8 discusses the condition of the tower internals following the testing in more detail.

TABLE 5-6. RELATIVE SATURATION OF CALCIUM SULFATE IN SCRUBBERS

Period	Module	$CaSO_4$ Relative Saturation Feed	Effluent
Baseline	S-1	1.12	1.20
	S-2	1.17	1.14
Adipic Testing	S-1	1.12	1.25
	S-2	1.12	1.25

5.3.6 Adipic Acid Consumption

Adipic acid was added to the system in the limestone sump (which also received product slurry from the ball mills). From the sump, the adipic-limestone mixture was transferred to the limestone storage tank and then fed to each module at a rate which was determined by a pH feedback control loop. The adipic acid exited the modules with the spent slurry that was discharged to the dewatering facility for solids disposal. Much of the adipic acid fed to the dewatering facility was recovered in the thickener or vacuum filter, and returned through the supernatant tank to the scrubbers.

Adipic acid was lost from the system in the following ways:

- In the liquid associated with the filter cake.
- In the solids in the filter cake (as a solid solution or occluded species).
- In fugitive liquid or slurry losses.
- In the chemical degradation of the adipic acid.

Two of these losses, the filter cake liquor losses and the fugitive losses, could be estimated from routine process measurements. Estimating the fugitive losses was important since the dewatering facility, designed to handle a calcium sulfite sludge, experienced difficulty in handling gypsum. Many of the upsets resulted in fugitive discharges of liquid and slurry containing adipic acid. These upsets were accounted for by measuring the quantity of makeup water fed to the system and comparing that to its theoretical water consumption. Despite a concerted effort to minimize the fugitive losses, results of these calculations show an average of about 40 gpm (0.15 m^3/min) of excess water fed to the FGD system ended up as fugitive discharges. In addition, not all of the water fed to the system was metered since a fire hose could be used to add water to the supernatant tank. Therefore, the 40 gpm (0.15 m^3/min) fugitive water loss rate is a conservative figure.

Table 5-7 presents the results of the adipic acid material balances performed for March and April. Two sets of adipic acid consumptions are shown. The first is the actual adipic acid added while the second has been corrected for adipic acid accumulation (or depletion) in the system (including losses of adipic acid associated with the estimated fugitive discharges). As mentioned earlier, the fugitive discharge rate was not completely accounted for, and therefore, the adjusted adipic acid number is a conservative estimate.

The adjusted actual-to-theoretical adipic acid ratio (defined as adjusted feed rate divided by the adipic acid exiting in the sludge (liqur) ranged from 6 during early April from 13 during March. The value for the early April period is significant since major efforts were made at this time to improve dewatering plant operations and decrease unmetered losses. The dewatering plant operated during the April 2 to 15 period with no major upsets in spite of the problems created by handling the gypsum in a system designed for sulfite.

TABLE 5-7. ADIPIC ACID MATERIAL BALANCE RESULTS

	March 11-30		April 2-15	
Adipic Acid Addition, lbs/hr (kg/hr)	190	(86)	110	(50)
Adjusted Adipic Acid Addition[a], lbs/hr (kg/hr)	120	(54)	80	(36)
Adipic Acid Losses in Sludge Liquor, lbs/hr (kg/hr)	9	(4)	13	(6)
Actual/Theoretical Ratio[b]	21		9	
Adjusted Actual/Theoretical Ratio	13		6	
Adipic Acid Consumption, lb/short ton SO_2 (g/kg SO_2)	41	(20)	29	(14)
Adjusted Consumption, lb/short ton SO_2 (g/kg SO_2)	25	(13)	18	(9)
Adjusted Cost (¢/kWh)[c]	0.041		0.029	

[a]The adipic acid addition was reduced by the amount of accumultation plus the adipic acid lost with fugitive water discharges.

[b]Acutal/Theoretical Adipic Acid Ratio = $\frac{\text{Actual Adipic Acid Added}}{\text{Adipic Acid Lost in Sludge}}$

[c]Assuming Adipic Acid at 60¢/lb ($1.33/kg)

A useful parameter when comparing results of adipic acid material balances is the quantity of adipic acid fed per amount of SO_2 absorbed. During early April, 18 pounds of adipic acid were consumed per ton of SO_2 absorbed (9g/kg). For March, the consumption rate was about 40 percent higher. While adipic acid consumption rates this high were not noted at Shawnee on occasion, the adipic acid consumption rates averaged 14 pounds per ton of SO_2 absorbed (7g/kg) in the runs performed at Shawnee used to simulate the Springfield forced oxidation tests [18].

Adipic acid addition rates were converted to cents per kilowatt-hour to examine the operating cost impact of adding adipic acid to the SWPP electricity production rate. The operating cost component would be as low as 0.029 cents per kilowatt-hour if the known fugitive liquid losses could be eliminated. This cost does not include capital expenditures for an adipic acid feed system nor does it give any credit to increases in limestone utilization and the reduced scaling and plugging potential in the tower mist elimination and internals. The cost of 0.029 cents per kilowatt-hour is less than 1 percent of the production cost of a kilowatt-hour at SWPP.

SECTION 6

NATURAL OXIDATION TEST PHASE

The effect of adipic acid addition on scrubber performance under natural oxidized conditions was examined during this phase of the demonstration program. Forced oxidation equipment was removed during the May plant outage, and both scrubber modules were converted back to their normal equipment configurations. In addition, Module S-1 was converted from a TCA tower to a perforated tray tower during the May outage. During the first portion of the natural oxidation test phase, both scrubbers were run without adipic acid to document baseline performance. Approximately two months of testing with adipic acid was then conducted to characterize the performance of adipic acid under natural oxidation conditions. This section describes the various tests performed, as well as the results from the natural oxidation test phase. Appendix C contains a data summary for the natural oxidation testing.

6.1 TEST PLAN

Table 6-1 shows the schedule for the natural oxidation test phase. Testing without adipic acid was conducted during the first three weeks to establish a baseline for later comparisons with operations using adipic acid. During the ensuing adipic acid testing, the adipic acid concentration and pH set points were varied to achieve the desired SO_2 removal goals. Although the process conditions were more varied for this phase than during the forced oxidation testing, the emphasis was still on operating with fixed set points for extended periods to determine the effect of adipic acid addition on the operation of full-scale FGD systems.

One objective of the natural oxidation testing was to define adipic acid requirements to achieve 85 percent SO_2 removal. This is approximately the SO_2 removal required at SWPP to meet their 1.2 lb $SO_2/10^6$Btu emission requirement. A second objective was to examine the operating conditions required to achieve 95 percent SO_2 removal. Approximately one month of testing was performed under the 95 percent removal test conditions.

TABLE 6-1. NATURAL OXIDATION TEST SCHEDULE

Period	pH	SO_2 Removal Goal	Adipic Acid Concentration
May 20 - June 12	5.0 to 5.8	Baseline	0
June 26 - July 13	5.4	85%	(Varied to Achieve the Desired SO_2 Removal Efficiency)
July 14 - July 21	5.5	95%	
July 21 - August 1	5.2	85%	
August 1 - August 11	5.5	85%	
August 11 - August 31	5.1 to 5.4	95%	

6.2 TEST RESULTS

The effects that adipic acid addition had on plant operation in the natural oxidation testing phase are evaluated based on the following key operating variables:

- SO_2 removal efficiency
- Limestone utilization
- Sulfite blinding
- Scaling potential
- Adipic acid consumption

6.2.1 SO_2 Removal

Figures 6-1 and 6-2 show the time phase relation between the adipic acid concentration and the SO_2 removal efficiency during each of the test periods. Overall, the SO_2 removal goals established were generally met throughout most of the test period. Note the strong relationship, in these figures, between SO_2 removal and the adipic acid concentration. There is a diminishing effect of increased adipic acid concentration once the SO_2 removal efficiency is greater than 90 percent. This trend would be expected with any contactor although the actual SO_2 removal response is closely tied to the gas-liquid contact limitations of a specific contactor.

Before discussing specific test results and correlations, some attention should be given to differences between the two scrubber modules during the natural oxidation test phase. During the May plant outage, Module S-1 was converted to a tray tower while S-2 remained a TCA. Thus, reasons for performance differences between the two modules were more difficult to determine during this phase of testing. Initially, Module S-2 achieved higher SO_2 removals than did S-1. The poorer performance of S-1 was caused by the module's lower gas-side pressure drop and resulting poorer gas-slurry contacting in the tray tower. After portions of the upper two perforated trays in S-1 were blocked off in July, both modules were operated at essentially the same pressure drop and achieved similar SO_2 removals. As testing continued, Module S-2 experienced some TCA sphere failure and a corresponding reduction in performance.

Table 6-2 presents the results of the natural oxidation testing. Module S-2 achieved a higher baseline removal than did Module S-1 due to the pressure drop differences discussed above. At a scrubber pH of 5.6, Module S-1 averaged 68 percent SO_2 removal compared to an average 72 percent removal with Module S-2.

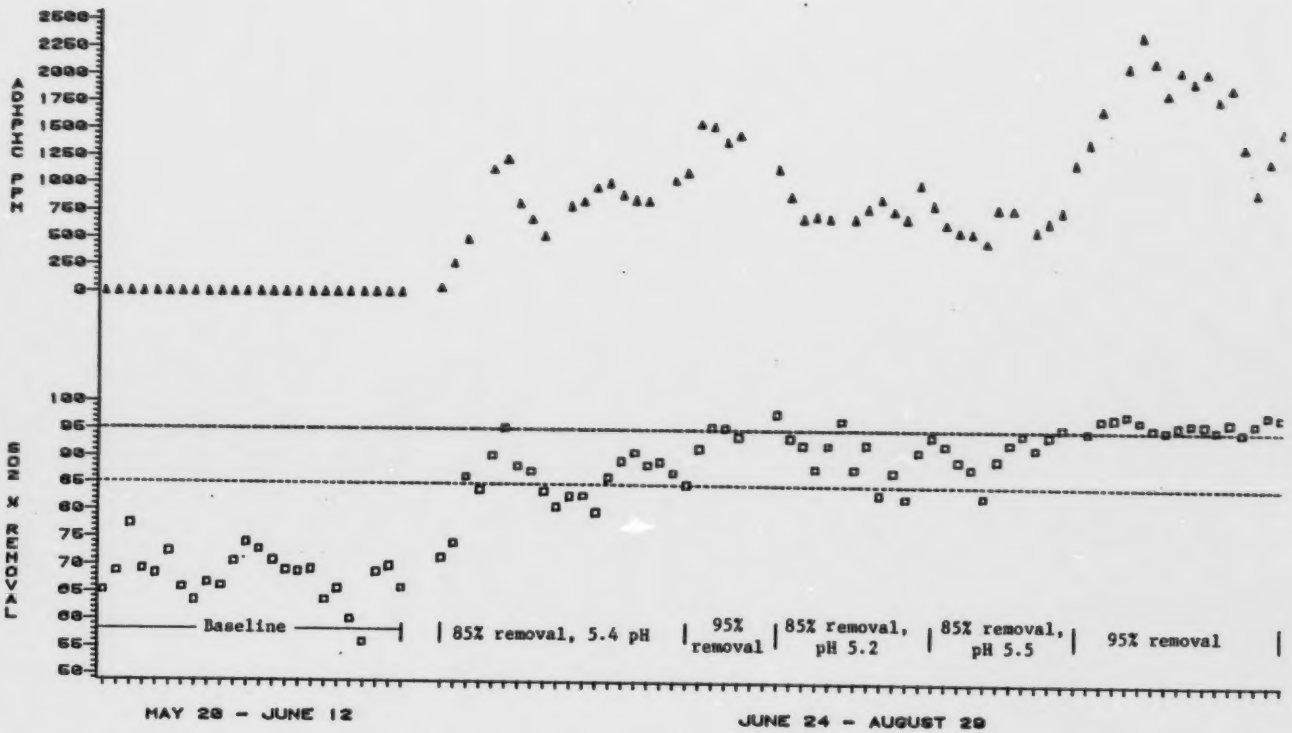


Figure 6-1. Summary of natural oxidation/adipic acid testing - Module S-1.

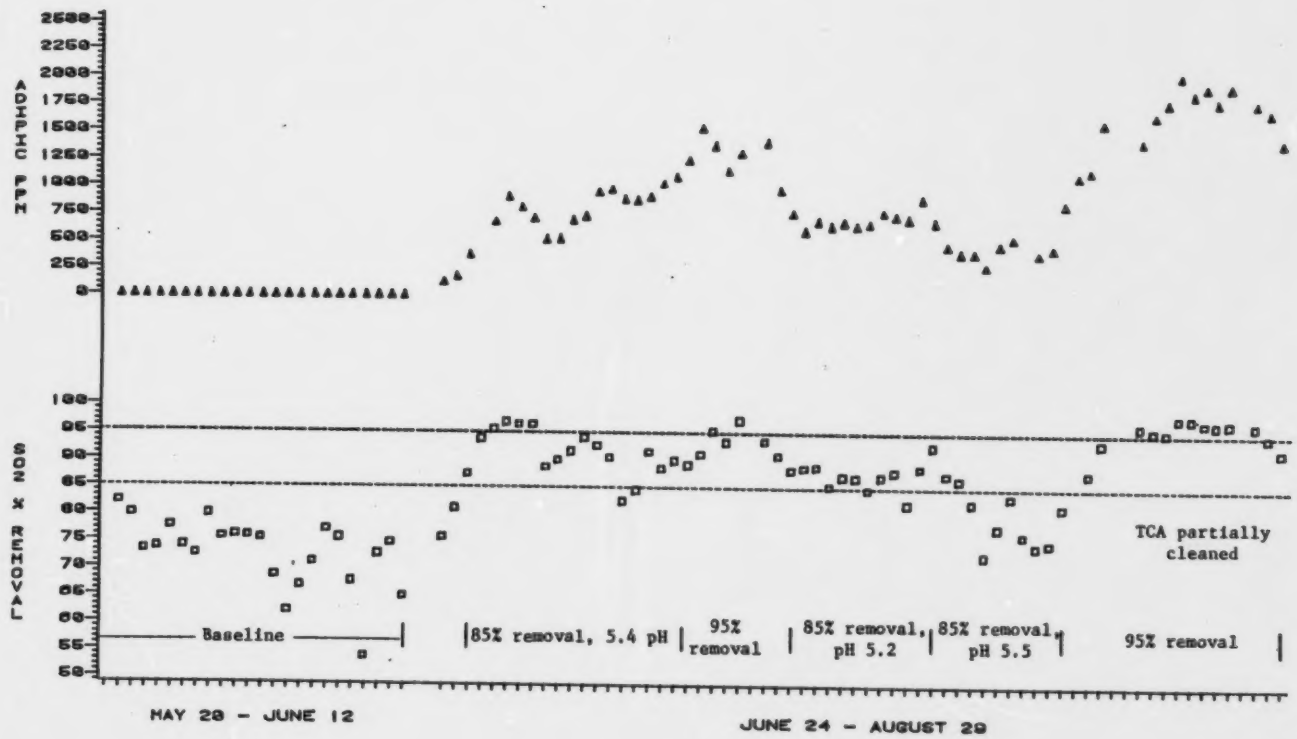


Figure 6-2. Summary of natural oxidation/adipic acid testing - Module S-2.

TABLE 6-2. SUMMARY OF NATURAL OXIDATION SO_2 REMOVAL RESULTS

	Operating Time (Days)	pH	Adipic Acid Conc. (ppm)	SO_2 Removal (%)
Tray Tower (Module S-1)				
Baseline*	24	5.6	0	68
Goal - 85% Removal[a]	17	5.4	1000	87
Goal - 85% Removal @ 5.2 pH	12	5.2	760	90
Goal - 85% Removal[b] @ 5.5 pH	10	5.5	640	91
Goal - 95% Removal[b]	17	5.4	1650	96
TCA Tower (Module S-2)				
Baseline	24	5.6	0	72
Goal - 85% Removal	17	5.3	890	91
Goal - 85% Removal @ 5.2 pH	12	5.2	700	88
Goal - 85% Removal[b] @ 5.5 pH	10	5.4	580	78
Goal - 95% Removal[b]	13	5.2	1590	94

[a]The void area in the tray tower was about 10 percent higher during these test periods than in the later test periods.

[b]These goals were obtained in the tray module but not in the TCA module. Deteriorating conditions in the TCA module and a common adipic acid addition system prevented the goals from being attained in the TCA module.

During the first 17 days of adipic acid testing in the 85 percent target removal period, Module S-2 (TCA tower) averaged 91 percent SO_2 removal at a pH of 5.3 and 890 ppm adipic acid concentration. Module S-1 removed less SO_2 (87 percent) at a slightly higher pH value (5.4) and adipic acid concentration (1000 ppm). Again, this was due to the lower pressure drop in the S-1 tower.

After the trays in S-1 were blocked off (which decreased the void area approximately 10 percent), Module S-1 averaged 90 percent removal at a pH of 5.2 and a 760 ppm adipic acid concentration. Module S-2 produced similar results with an average SO_2 removal of 88 percent at a pH of 5.2 and 700 ppm adipic acid concentration. The target removal during this 12-day period was 85 percent. Actual removals averaged slightly higher, however, due to increased SO_2 removal during lower load periods.

Following this 12-day period, differences in the scrubbers' performance again became apparent during the 85 percent removal 5.5 pH testing. This time, however, Module S-2 began experiencing significantly lower SO_2 removals than S-1. Subsequent examination near the end of the adipic acid test period showed that a high temperature excurstion had caused the TCA spheres to break, fill with slurry, and eventually plug the TCA cages. Normal attrition of the spheres also contributed to this problem. As Table 6-2 shows, Module S-2 achieved only 78 percent SO_2 removal compared to Module S-1's average SO_2 removal of 91 percent. While S-1's pH values and adipic level were slightly higher than S-2's, these differences are not significant enough to explain the variation in the two SO_2 removals.

The final goal during the natural oxidation testing was to achieve 95 percent SO_2 removal over a period of several weeks. As shown in Table 6-2, Module S-1 averaged 96 percent removal at a pH of 5.4 and a 1650 ppm adipic acid concentration over a 17-day period.

During this 95 percent removal testing, Module S-2 was taken off line and examined for sphere damage. As mentioned previously, significant pluggage of the TCA cages with limestone slurry and slurry filled TCA spheres was discovered. Since Module S-2 was due to be converted to a tray tower during a scheduled plant outage in October, extensive cleaning and a complete recharging of the sphere cages (which would have required the purchase of additional TCA spheres) could not be justified. Instead, the remainder of the new spheres on hand were used to replace the most damaged spheres. To the extent that time would allow, the plugged TCA cages (although not all of them) were also cleaned.

This maintenance improved the performance of S-2 for the remainder of the adipic acid addition phase. During the last 10 days of the 95 percent SO_2 removal period, S-2 averaged 96 percent removal at a pH of 5.2 and a 1750 ppm adipic acid concentration and a 94 percent removal over the entire 13 day test period. Over the last 10 days of adipic acid testing, Module S-1 also averaged 96 percent SO_2 removal at a pH of 5.3 and a 1740 ppm adipic acid concentration.

Since Module S-1 was converted to a tray tower and Module S-2 suffered from reduced performance through a significant portion of the testing, there are difficulties comparing the full-scale results directly with the Shawnee prototype results. This is further complicated by the fact that most of the correlations reported for prototype natural oxidation testing have been derived from high pH runs (scrubber pH values higher than 5.6). Spot checks of the Springfield data, taken when the TCA was operating at a high pH before sphere damage, indicate that the Shawnee correlations predict full-scale results reasonably well. As in the forced oxidation testing, the prototype correlations again predict slightly higher SO_2 removals than those actually achieved.

The data from the tray tower in the demonstration program were fit to the following equation:

$$\text{Fractional } SO_2 \text{ Removal} = 1 - \exp\{-0.00131\ Ad - 0.00216\ \exp(pH) - 0.0996\ L/G\} \quad (6\text{-}1)$$

where Ad = the adipic acid concentration expressed as ppm,

pH = the scrubber feed pH, and

L/G = the liquid-to-gas ratio expressed as gal/1000 acf.

Figure 6-3 shows the agreement between the actual SO_2 removal and the removal predicted from Equation 6-1. This equation was developed to describe the trends noted during the program, and caution should be applied in using the equation since parametric testing was not performed during the demonstration. Note that the liquid and gas rates were included in Equation 6-1 and were clearly important variables in SO_2 removal during natural oxidation testing. Due to data scatter and the relatively small range of SO_2 removals resulting from the 95 percent removal goal, the effect of L/G was not observed in the forced oxidation test data.

To summarize, the natural oxidation testing showed that the tray tower could achieve 95 percent SO_2 removal at full load conditions with a scrubber feed pH at 5.2 to 5.3 and a 1700 to 1800 ppm adipic acid concentration. A higher pH and slightly lower adipic acid concentration could also achieve 95 percent removal although limited testing was performed under these conditions. Greater than 85 percent SO_2 removal can be achieved with a variety of pH and adipic acid concentration set points. At a pH of 5.2, an adipic acid concentration of 700 to 800 ppm resulted in 85 percent SO_2 removal while a 600 to 700 ppm adipic acid concentration of a pH of 5.5 resulted in the same removal. The TCA Module achieved similar SO_2 removal efficiencies under similar operating conditions while it was performing well. However, damaged TCA spheres and resulting plugged TCA beds reduced the TCA performance through a substantial portion of the testing.

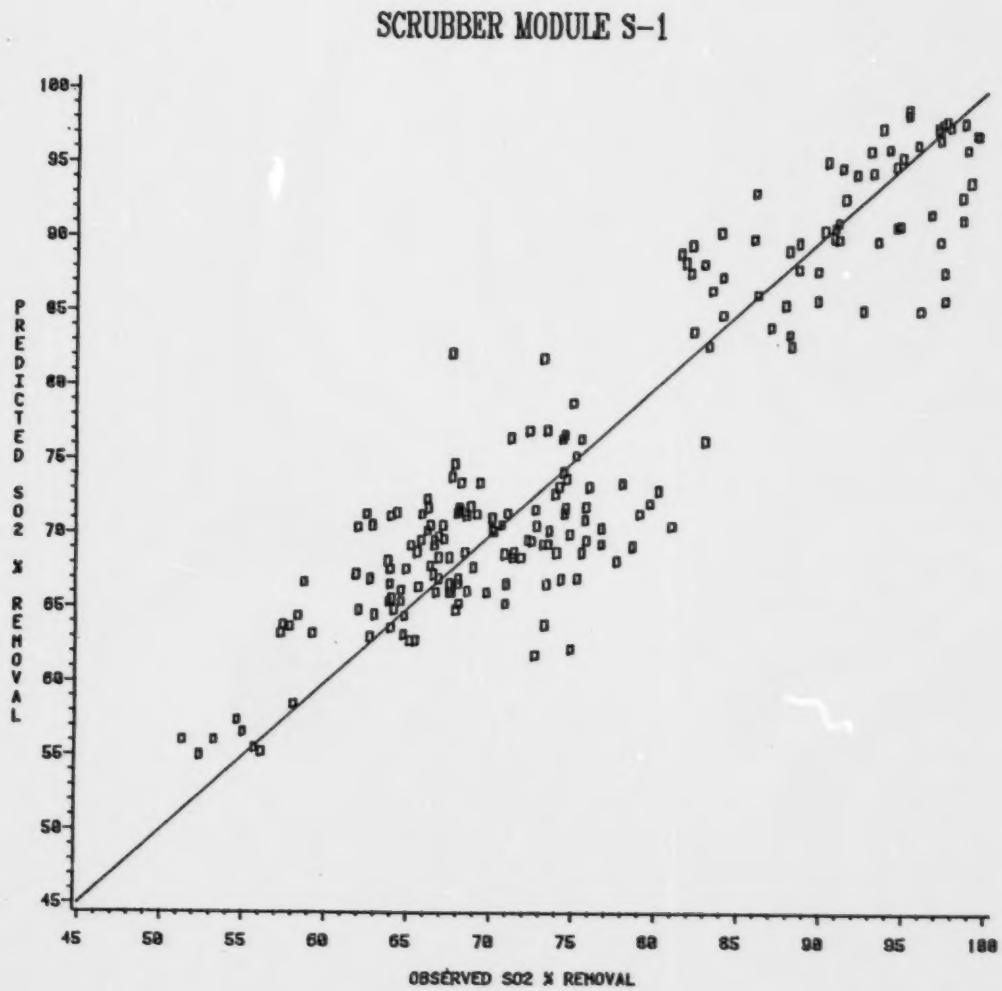


Figure 6-3. Fit of Springfield tray tower data to model.
Removal = 1 - exp[-.00131 Ad - .00216 exp(pH)
- .00996 L/G]

6.2.2 Limestone Utilization

Table 6-3 shows that improved utilization was achieved with adipic acid addition. (Table 6-3 presents average pH values and average utilizations for each test period). The adipic acid buffering action allows the system to operate with a relatively low reaction tank pH, promoting good limestone utilization, while simultaneously achieving good SO_2 removal.

TABLE 6-3. SUMMARY OF LIMESTONE UTILIZATION RESULTS

	pH	Utilization (%)
Tray Tower		
Baseline	5.6	79
Adipic Acid Testing		
85% Removal Goal	5.4	81
85% Removal Goal	5.2	86
95% Removal Goal	5.4	78
TCA Tower		
Baseline	5.6	69
Adipic Acid Testing		
85% Removal Goal	5.3	92
85% Removal Goal	5.2	82
85% Removal Goal	5.4	75
95% Removal Goal	5.2	86

Operating pH values had the most obvious effect on limestone utilization during the natural oxidation testing. Figure 6-4 indicates a very strong correlation between scrubber feed pH values and limestone utilization during the baseline testing. The correlation was not as good during the adipic acid test period. Figure 6-5 shows a comparison between the baseline correlation and adipic acid test results. The adipic acid test data are more scattered than the baseline test data for a number of reasons;

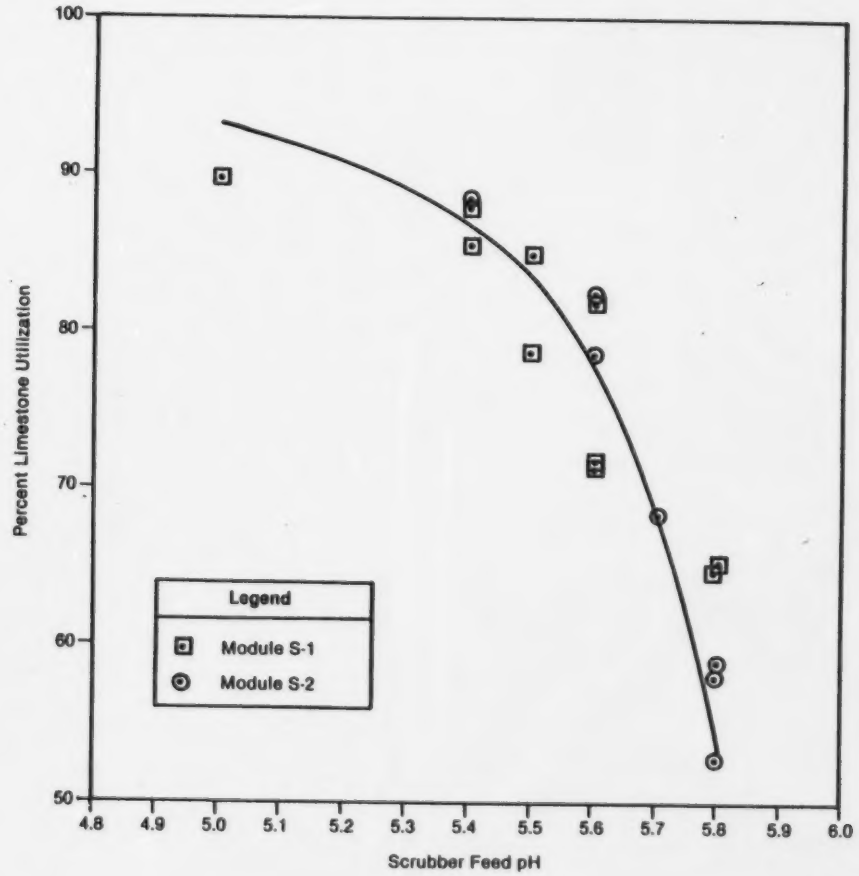


Figure 6-4.
Percent Limestone Utilization versus Scrubber Feed pH - Without Adipic Acid

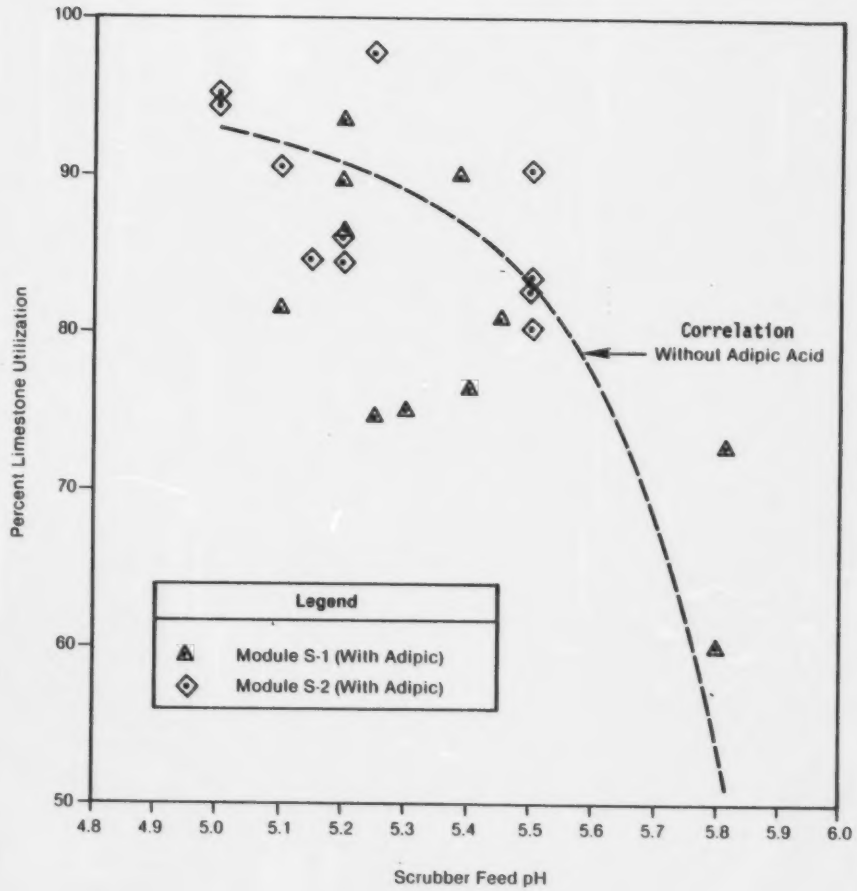


Figure 6-5.
Percent Limestone Utilization versus Scrubber Feed pH - With Adipic Acid

1. There may have been periods of sulfite blinding (discussed in Section 6.2.3) that were not identified and corrected which may have resulted in low limestone utilizations at relatively low pH values.

2. Fluctuations in scrubber pH during the 24-hour period before adipic acid addition sampling may have a dramatic effect on the measured limestone utilization. Scrubber pH values were much more stable prior to sampling during baseline testing than they were prior to sampling during the adipic acid testing.

3. Different adipic acid concentrations resulted in different SO_2 removal efficiencies and different solid phase residence times. Residence times can have an effect on limestone utilization, and this variable is not accounted for in Figures 6-4 and 6-5.

6.2.3 Sulfite Blinding

Sulfite blinding on limestone particle surfaces caused problems during the natural oxidation phase which were similar in some ways to those encountered during forced oxidation testing (Section 5.3.4). For instance, blinding episodes seemed to occur most frequently immediately after unit load increases.

However, marked differences were noted in the sulfite blinding episodes during the two test phases. During forced oxidation, rapid decreases in reaction tank pH, decreases in SO_2 removal efficiency, and increases in the limestone feed rate accompanied the onset of limestone blinding. During natural oxidation testing, blinding also resulted in increased limestone consumption as calcium sulfite coated the limestone surface. However, the reaction tank pH did not drop rapidly as during forced oxidation testing, nor was the SO_2 removal markedly affected. Rather, the pH values dropped only slightly, and reaction tank pH control became sluggish. The subtle changes in the pH values and SO_2 removal efficiencies made blinding more difficult to identify during natural oxidation testing. After some extended blinding episodes, the limestone feed could be turned off for several hours with no effect on reaction tank pH values.

Changes in limestone feed rate had little effect on reaction tank pH values, possibly because the sulfite-bisulfite shift is sensitive to pH in the 5.4 to 5.5 pH range. As the pH decreases, the calcium sulfite layer on the limestone surface seems to dissolve exposing a fresh calcium carbonate surface. However, as the calcium carbonate dissolves, the pH around the particle again rises, the bisulfite shifts back to sulfite, and again precipitates as calcium sulfite on the limestone particle.

Although sulfite blinding during natural oxidation was initially difficult to identify, experience was gained as the testing progressed. However, a more sophisticated reagent feed control than a simple pH feedback system would be beneficial in reacting to blinding problems. A system which automatically senses pH responsiveness or a feed forward system based on inlet flue gas flow and SO_2 content with pH feedback for trim purposes are systems which could offer improvements.

6.2.4 Chemical Scaling

Scaling was monitored throughout the program, both by chemical analysis and visual inspection. Incipient scaling was not noted in either scrubber module, but solids deposition and plugging was a problem in the mist eliminator sections and in the TCA after sphere failure.

Gypsum relative saturation was used to measure the system's scaling tendency during natural oxidation in a manner similar to that discussed for the forced oxidation testing (Section 5.3.4). Throughout the testing, relative saturation averaged between 1.1 and 1.2 in the effluent streams from both modules and only seldom approached the 1.3 to 1.4 scaling region. At no time did the gypsum relative saturation exceed 1.4.

As indicated by the relative saturations determined, no major scaling occurred in either module during the testing. The TCA module did experience contactor sphere failure which resulted in solids settling on the

immobile spheres. This sphere failure ultimately caused pluggage severe enough to adversely affect module performance and to necessitate an unscheduled module shutdown for cleaning. Some crystal growth occurred on the settled solids but no evidence was found of incipient chemical scaling directly on contactor surfaces.

Some gypsum solids were observed on the bottom tray of the S-1 module. However, no pluggage or increase in pressure drop was noted and the solids were easily cleaned when the scrubber was brought off-line in September. One small portion of the bottom tray was plugged with solids, but this appeared to be a wet/dry interface problem.

The major problem areas with scaling and plugging during natural oxidation testing were in the mist eliminators of both modules. Some gypsum scaling was noted at the end of forced oxidation testing, although the buildup was quite minimal. However, during the natural oxidation testing, the buildup was severe enough to restrict flue gas flow and cause a system shutdown for cleaning. The main cause of the mist eliminator problems seemed to be plugged wash nozzles. Thickener overflow is used for mist eliminator washing and dewatering excursions evidently filled the mist eliminator wash circuit with solids, which effectively plugged the wash nozzles and limited wash water flow. Once solids were collected on mist eliminator surfaces, SO_2 absorption across the mist eliminator apparently caused calcium carbonate and sulfite solids dissolution resulting in the precipitation of gypsum. This formation of gypsum cemented the softer solids in place and provided additional sites for continued gypsum crystal growth. To compound the problem, the thickener overflow liquor is already saturated with respect to gypsum, so the small amount of wash water which reached mist eliminator surfaces did not help much in reducing gypsum buildup. Gas flow maldistribution through the modules may have also contributed to the mist eliminator pluggage problem. However, the major problem was thought to be the poor washing of the mist eliminators due to plugged nozzles and washing with water with a high solids content.

The difference in limestone utilization between forced oxidation and natural oxidation testing should be emphasized in discussing the mist eliminator scaling and plugging problems. For most of the forced oxidation period, the scrubber feed pH set point was 5.2 or lower, which resulted in limestone utilizations in the 90 percent range. In natural oxidation, a wider range of pH set points was employed with a corresponding wider range of limestone utilizations. The presence of higher amounts of calcium carbonate carried to the mist eliminator may have contributed to the gypsum scaling. As discussed previously, once gypsum scaling is initiated, continued crystal growth on the initial scale compounds the problem. However, the wash loop pluggage problems makes direct comparison between mist eliminator performance during forced and natural oxidation difficult.

6.2.5 Adipic Acid Mass Balance

As discussed in the Forced Oxidation Section (Section 5), adipic acid left the FGD system:

- in the liquid associated with the filter cake,
- in the filter cake solids as a coprecipitate or occluded species,
- in the fugitive liquid or slurry losses, and
- in the chemical degradation of adipic acid.

The adipic acid lost with filter cake in the liquid and solid phases can be estimated from the SO_2 absorbed (estimate of sulfur solids production rate) and the adipic concentrations in the filter cake solids and associated liquor. Fugitive water losses are very difficult to estimate since these water losses are not metered. Undesired fugitive discharges of liquid and slurry which contained adipic acid were less prevalent than during forced oxidation testing, but still proved to be a problem at times during the natural oxidation testing. The quantities of liquor discharged were low enough during natural oxidation testing so that water balances could not accurately quantify

the losses, but these discharges may be significant with regards to adipic acid material balances. Since chemical degradation of the adipic acid is calculated based upon the difference in the adipic acid added and the known adipic acid losses, and since it was not possible to accurately quantify the fugitive losses, degradation and fugitive losses are considered together.

Table 6-4 presents the adipic acid material balance results for the natural oxidation testing. As shown, the adipic acid addition rate increased substantially when the SO_2 removal efficiency was increased from 85 to 95 percent. The higher addition rate reflects the higher adipic levels reqired to achieve 95 percent removal and subsequent increased adipic acid losses in the filter cake and increased degradation at higher adipic concentrations. Adipic acid losses in the filter solids and liquor were 12 and 9.6 lbs/hr (5.4 and 4.3 kg/hr) respectively, at 85 percent SO_2 removal. At 95 percent removal, these losses increased to 37 and 21 lbs/hr (16.7 and 9.5 kg/hr) in the solids and sludge liquor, respectively.

TABLE 6-4. ADIPIC ACID MATERIAL BALANCE RESULTS FOR THE NATURAL OXIDATION TESTING

	85% Removal		95% Removal	
Adipic Acid Addition[a], lbs/hr (kg/hr)	46	(21)	113	(51)
Adipic Losses in Sludge Liquor, lbs/hr (kg/hr)	9.6	(4.3)	21	(9)
Adipic Losses in Sludge Solids, lbs/hr (kg/hr)	12	(5)	37	(17)
Adipic Degradation and Fugitive Water Losses, lbs/hr (kg/hr)	20	(9)	55	(25)
Actual/Theoretical Ratio[b]	4.8		5.4	
Adipic Acid Consumption, lb/ton SO_2 (g/kg SO_2)	11	(5.5)	29	(14.5)
Cost[c] (¢/kWh)	0.017		0.047	

[a]The adipic acid addition was reduced by the accumulation.

[b]Actual/Theoretical Adipic Acid Ratio = $\frac{\text{Actual Adipic Acid Added}}{\text{Adipic Acid Lost in Sludge Liquor}}$

[c]Assuming adipic acid at 60¢/lb ($1.33/kg)

Perhaps the most significant result shown in Table 6-4 is the adipic acid consumption. To attain 85 percent removal, approximately 11 lbs adipic/ton SO_2 (5.5 g/kg) removed had to be added to the system. Likewise, 29 lbs adipic/ton SO_2 (14.5 g/kg) was required to achieve 95 percent removal. This corresponds to an adipic acid addition operating cost of 0.017¢/kWh at 85 percent and 0.047¢/kWh at 95 percent SO_2 removal. These costs are based upon an adipic acid price of 60¢/lb (1.33/kg) and do not include any capital expenditures for an adipic feed system. These costs also do not reflect credit for increases in limestone utilization, decreased sludge volumes, or the associated decreased potential for scaling in the absorber towers and mist eliminators.

SECTION 7

DIBASIC ACID TEST PHASE

Dibasic acids (DBA), a by-product in the production of adipic acid, can be used in much the same way as adipic acid to enhance SO_2 mass transfer in a limestone scrubber. A thirty-day performance test was conducted at SWPP with a quantity of DBA material provided by Monsanto. The material consisted of an aqueous mixture of adipic, glutaric, and succinic acid. The combined concentration of the organic acids varied from 21 to 24 percent by weight in the shipments received over the course of the test period. The DBA was fed into the FGD system at the same point that adipic acid was added, the limestone ball mill product sump.

7.1 TEST PLAN

The objective of the DBA testing was to gather data similar to those gathered during the adipic acid/natural oxidation testing. Information on the operation and performance of the SWPP FGD system at both the 85 and 95 percent SO_2 removal level was desired. The duration of the DBA test was not as long as that for the adipic testing since the scrubbers' SO_2 removal performance was not expected to vary substantially using DBA instead of adipic acid. Test results from the EPA pilot scrubber in Research Triangle Park had shown virtually the same removal efficiencies for equivalent concentrations of DBA or adipic acid in the scrubbing liquor[19]. The one month test was also intended to identify any operating problems associated with the use of DBA and to determine the DBA loss rate from the systems.

Following the completion of adipic acid testing, one week was needed to drain and purge the system of adipic acid before DBA was added. One month

of testing was then planned with the DBA material (September 7 to October 7, 1981). The 85 percent SO_2 removal testing was performed to determine the conditions necessary to maintain the SWPP unit in compliance. This testing lasted for 18 days (from September 7 to September 24). From September 25 to October 7, the DBA feed rate was increased to maintain a 95 percent SO_2 removal efficiency.

7.2 DBA TEST RESULTS

The results of the 30-day test with DBA are summarized in this section. Operating conditions and SO_2 removal efficiency goals were set so that a comparison between these results and those from the earlier natural oxidation testing could be made. Detailed results of the testing (in the form of data plots) are included in Appendix C.

7.2.1 SO_2 Removal

Table 7-1 shows the average SO_2 removal of each module during the two DBA testing periods.

TABLE 7-1. AVERAGE SO_2 REMOVAL FOR DBA TESTING

Test Period	Average Scrubber Feed	Average DBA Conc. (ppm as Adipic Acid)	Average SO_2 Removal %
85% SO_2 removal			
Module S-1	5.4	480	90
Module S-2	5.4	420	78
95% SO_2 Removal			
Module S-1	5.4	1310	96
Module S-2	5.4	1020	94

Module S-1 routinely achieved the SO_2 removal goals over the 30-day test period with DBA. It averaged 90 percent removal during the 85 percent goal tests, and 96 percent during the 95 percent goal tests. The module averaged better than the 85 percent removal goal because the objective of this test was to maintain the unit in compliance with the 1.2 lbs SO_2 per 10^6Btu standard. To do this, conditions were maintained in the module which would keep emissions below this ceiling with the unit operating at full load. Variations in Module S-1 resulted in SO_2 removal efficiencies as high as 96 percent when the unit operated at half load. During the high load periods, the S-1 SO_2 removal efficiency would typically drop to around 83 to 84 percent, which for the particular coal sulfur content being burned, resulted in an emission rate of about 1.0 to 1.1 lbs $SO_2/10^6$Btu. Likewise, during the 95 percent removal testing, the SO_2 removal increased to above 98 percent when the system was operated at lower loads.

Throughout the DBA test period, the performance of Module S-2 was below that of Module S-1. The poor condition of the ball charge inside the TCA tower was responsible for the lower performance of Module S-2. Following the completion of the October testing, Module S-2 was examined, and almost one-half if its sphere cages were found to be either plugged with solids or without spheres. Module S-1's trays were found to be in good shape. In mid-September, S-1 had been taken off-line and the solids which had built up on the bottom of the lowest tray were removed. No noticeable increase in removal efficiency occurred at the time, nor was any expected since only about 10 percent of the lower tray's open area had been blocked. Because City Utilities was planning on converting Module S-2 to a tray tower less than a month after the end of the DBA testing, extensive improvement involving replacing and redistributing its sphere charge could not be justified. For this reason, the DBA feed rate was controlled to maintain Module S-1 at the target removal levels. This resulted in relatively poor performance for Module S-2 as evidenced by the lower removal efficiencies observed during the test period.

The difference between the two modules was less significant during the 95 percent removal testing. Considering the fact that Module S-2 operated at generally lower DBA concentrations, the difference in performance between the two if operating under the same conditions would probably be even less. One major reason for the apparent improvement in the performance of Module S-2 is that much lower gas flows were fed to the module during the latter stages of testing. This increases the L/G thereby increasing the SO_2 removal efficiency.

The values reported in Table 7-1 for DBA concentrations over the test period are as equivalent adipic acid concentrations. The buffer capacity analytical technique used to track the liquid-phase DBA in the reaction tank was developed as part of the demonstration program. The difficulty in determining the DBA concentration stems from the presence of a mixture of adipic, glutaric, and succinic acids in the system. This prevents using ion chromatography (IC) as the primary analytical tool, since peaks of the adipic-glutaric-succinic mixture in the sample cannot be separated easily. Ion chromatography exclusion (ICE) techniques can make this determination, but this technique is a more time consuming effort. The buffer capacity technique measures the buffering capacity of all buffers regardless of the source. Another purpose of developing the buffer capacity technique was to provide personnel at FGD facilities using adipic acid or any mixture of mono- or dibasic acids with an accurate, low cost, and relatively fast method for monitoring the level of organic acid at any point in the system. The technique basically consists of an acid-base titration over the buffer range of most organic acids that would be used as additives and is explained in detail in Appendix B.

Comparisons and results from the adipic acid test phase with the DBA test phase shows that equivalent SO_2 removal efficiencies were achieved with about 25 percent lower buffer capacities during DBA testing. This can be at least partially explained by lower average unit loads during DBA testing. (Operations subsequent to the completion of this program have shown that equivalent DBA or adipic acid buffer capacities are required to achieve equivalent removals with the system operating at the same load conditions.

7.2.2 Limestone Utilization and Sulfite Oxidation

Table 7-2 presents the results of the limestone utilization and sulfite oxidation measurements made during the DBA testing. The limestone utilization showed very little variation over the test period. Reaction tank pH was controlled at 5.4 throughout the test. The 80 to 82 percent average utilization for both modules is in the range seen for limestone utilization during the adipic testing at the 85 percent SO_2 removal level and at reaction tank pH values of 5.3 to 5.4. No utilization or oxidation measurements were made at the 95 percent removal level during the DBA testing.

TABLE 7-2. LIMESTONE UTILIZATION AND SULFITE OXIDATION DURING DBA TESTING

Module	Limestone Utilization %	Sulfite Oxidation %
S-1	80	27
S-2	82	26

The sulfite oxidation averaged somewhat higher percentages during the DBA testing than during adipic acid natural oxidation testing. The reason may be due to the vanadium content in the DBA fed to the system. Vanadium levels as high as 200 ppm have been reported in the mixture. The metal could act as a catalyst in promoting the sulfite oxidation reaction. The quality of the solids from the vacuum filter were noticeably improved during the DBA testing compared with the filter solids during the natural oxidation testing. The solids content of the dewatered sludge increased from an average of 53 percent during the adipic acid natural oxidation testing at 85 percent SO_2 removal, to an average of 57 percent during the DBA 85 percent removal testing. While this alone would not account for the improved handling properties of the filter cake, other factors could have contributed. These include more consistent sulfite oxidations and limestone utilizations for the DBA 85 percent removal test period compared to those observed during the adipic acid test period.

7.2.3 Chemical Scaling

The gypsum relative saturation remained equal to or below 1.3 in both the scrubber feed and scrubber effluent streams throughout the DBA testing. This indicates that incipient nucleation and scaling were not likely to have occurred on the towers during this test period. Section 8 discusses the condition of the internals of the two towers after the DBA testing. Briefly, solids were found in Module S-1 on the mist eliminators and on the bottom of the lowest tray. The solids on the chevron blades appeared to be gypsum scale, much of which was due to operation for over a week with no mist eliminator washing. The solids on the tray appeared to be due to the wet-dry interface occurring on the tray. Module S-2 had also experienced plugged mist eliminator wash nozzles and, as a result, had significant gypsum scale on the blades. Solids buildup in the sphere cages continued as observed during the adipic acid testing, but this buildup did not appear to have been initiated by chemical scaling. It appeared as though the spheres had failed and then filtered solids from the slurry causing pluggage of some of the cages. No other significant scale buildup was seen in the contacting section of either tower.

7.2.4 Dibasic Acid Mass Balance

DBA was added to the system on a continuous basis. The feed rate was controlled based on the results of daily liquid phase DBA concentration measurements and routine observations of the SO_2 removal performance of Module S-1. The DBA addition point was the same as for the aidpic acid additions in the ball mill product slurry sump which feeds directly into the limestone slurry storage tank (Figure 3-1). Some interruptions in feeding were experienced when the DBA crystallized from solution and blocked the flow. In addition, on cool nights (below 70°F) when crystallization was a problem, the feed would be shut off. Sufficient DBA was added during the day shift to maintain SO_2 removal efficiency.

Table 7-3 presents the results of the mass balance calculations for the DBA 85 percent and 95 percent SO_2 removal test periods. The results are presented in several ways to facilitate comparison with the adipic testing results. The DBA addition rate is the average rate that the material was added to the system over the period of the test. This rate is affected by such factors as the average unit load and number of hours the modules operated during the test period. Because both the load and fraction of time the modules were on-line differed between the 85 percent adipic acid testing and the 85 percent DBA testing, the average addition rates of the buffers is not the best way to compare the buffer feed requirements of the two systems. This was also the case for the 95 percent test periods. To compensate for these differences, the quantities of additive fed were normalized to a unit amount of SO_2 absorbed. This number was calculated by dividing the total buffer fed by the total SO_2 absorbed in each period.

TABLE 7-3. DBA MATERIAL BALANCE RESULTS

	85% Removal		95% Removal	
DBA Addition Rate, lbs/hr (kg/hr)	51	(23)	140	(63)
DBA Losses in Sludge Liquor, lbs/hr (kg/hr)	4	(1.8)	10	(4.5)
Acutal Theoretical Ratio[a]	13		14	
DBA Consumption, lb/short ton SO_2 removed, (g/kg)	15	(7.5)	39	(19.5)
Cost (¢/kWh)[b]	0.012		0.029	

[a]Actual/Theoretical Ratio = Actual amount of DBA added/DBA lost in the sludge liquor

[b]Cost of DBA based on 30¢/lb (67¢/kg) delivered SWPP.

DBA was consumed at about a 35 percent higher rate than adipic acid was during equivalent operation (see Table 6-3 for adipic acid consumption). At 85 percent SO_2 removal, 15 pounds of DBA were consumed per ton of SO_2 (7.5 kg/ton) removed compared to an adipic acid consumption of 11 pounds per ton of SO_2 (5.5 kg/ton) removed. Likewise, during 95 percent removal

testing, 39 pounds of DBA compared to 29 pounds of adipic acid per ton of SO_2 removed were consumed. The reason for the higher consumption rates can be seen by comparing the Actual to Theoretical Ratios. The ratio is a measure of the unaccounted for losses of buffer by chemical degradation, occlusion or coprecipitation in the solids, or fugitive leaks and spills. The larger the number, the greater the unaccounted for losses. There is a substantial increase in this ratio for the two DBA test periods (13 and 14) compared to the respective adipic test periods (4.8 and 5.4). Since fugitive losses were not significantly different between the tests, this indicates that the DBA material is subject to higher degradation rates and/or occlusion-coprecipitation. Analysis of the scrubber liquor by ion exclusion chromatography showed that there was very little of the succinic acid (<10 ppm) present in the liquid phase. Succinic normally made up about 25 percent of the feed on a weight basis. An analysis of the sludge solids showed that most of the succinic was associated with the solids. These analyses indicate that much of the difference between the adipic and DBA feed rates could be due to the loss of succinic acid via occlusion or coprecipitation with the solids.

Table 7-3 also presents the cost of the DBA material as it would impact the production cost of electricity at SWPP for the two levels of SO_2 removal efficiency. This number is calculated by dividing the cost of the DBA added over the period (assuming \$0.30/pound (\$0.67/kg) of material delivered) by the number of kilowatt-hours produced in the period. Despite the higher feed rates required for DBA, it is still less expensive than aidpic acid in the SWPP application for both SO_2 removal levels (0.012 ¢/kWh for DBA compared to 0.017 ¢/kWh for adipic acid at 85 percent SO_2 removal). It should be pointed out, however, that the parameters on which these cost calculations are based are site specific and would not necessarily be indicative of costs at another FGD facility.

SECTION 8

EQUIPMENT PERFORMANCE

This section summarizes the availability and performance of the limestone scrubbing system equipment during the adipic acid demonstration program. The reliability of the scrubbing system are discussed in Section 8.1 as well as the problems which led to scrubber outages. Equipment limitations and necessary modifications are described in Section 8.2. Finally, several examinations of the internals of the scrubber modules were performed during the forced oxidation, natural oxidation, and DBA testing. The results of these examinations are presented in Section 8.3.

8.1 SYSTEM RELIABILITY

Table 8-1 shows the boiler, scrubber, and continuous monitoring equipment reliability during the adipic acid demonstration program. Reliability is defined as the hours operated divided by the hours called on to operate. During the adipic acid test period (January 10 to August 31, 1981), the boiler operated 99 percent of the time it was called on to operate. Scrubber Modules S-1 and S-2 were 79 and 77 percent reliable, respectively. All continuous monitors (DuPont SO_2 and Thermox O_2 analyzers) were operational 83 percent of the time required. However, the SO_2 monitors alone achieved a reliability rating of 94 percent.

Similarly, Modules S-1 and S-2 were reliable 98 and 69 percent of the time during the DBA testing (September 7 to October 7). The overall monitoring system was 97 percent reliable, with the SO_2 monitors available all but one hour over this testing period.

TABLE 8-1. BOILER SCRUBBER, AND CONTINUOUS MONITORING SYSTEM RELIABILITY DURING ADIPIC ACID DEMONSTRATION PROGRAM

Period	Boiler	Scrubbers		Continuous Monitoring System	
		Module S-1	Module S-2	All Monitors	SO_2 Monitors Only
Average for 1979	-	34	42	-	-
Average for 1980	-	59	31	-	-
January 10-31	99.6	66	85	100	100
February	99	54	35	100	100
March	95.7	88	81	81	81
April	100	67	97	66	88
May	99.7	87	66	50	100
June	99.5	78	74	92	99.8
July	100	94	94	97	97
August	100	90	80	91	91
Average January 10-August 31	99	79	77	83	94
Average March 10-August 31	99.8	86	87	80	93
DBA Testing					
September 7-October 7	100	98	89	97	99.9

During 1979, Modules S-1 and S-2 were operated 34 and 42 percent of the time required. Likewise, in 1980 S-1 and S-2 were 59 and 31 percent reliable, respectively (Table 8-1). Thus, the scrubber reliabilities during the adipic acid demonstration represent a significant improvement over 1979-1980 reliabilities. Disregarding the first two months of the test period (during which significant downtime resulted due to weather related problems and initial scrubber adipic acid operating procedure shakedown), the reliabilities of S-1 and S-2 were 86 and 87 percent, respectively.

Adipic acid (or DBA), however, was not solely responsible for the improved reliability of the FGD system. Mechanical changes implemented by City Utilities, some revised process operating procedures, and additional process engineering input from test program personnel were also major factors in improving the overall system reliability. Some of the major changes leading to improved FGD system reliability at SWPP are shown in Table 8-2. A more detailed description of the equipment modifications and limitations is presented in Section 8.2.

TABLE 8-2. SUMMARY OF CHANGES TO IMPROVE FGD SYSTEM RELIABILITY

- Replaced FRP (plastic) pipe with lined steel pipe for added strength and improved heat tracing for freeze protection.
- Used clear liquor for cooling the flue gas in the presaturator instead of collected mist eliminator wash water.
- Revised the limestone feed loop to include an automatic water flush to remove limestone slurry when flow stopped.
- Made several changes in the dewatering plant including (1) 24 hour operation and maintenance, (2) larger drive motor for the pug mill that mixes the filter cake and fly ash, and (3) installation of a separate return line to the thickener for the filtrate.
- Replaced inlet isolation damper drive motors with larger ones.
- Reduced the on-off cycling of the scrubbers by cooperative system load management.
- Decreased the sphere charge in the two towers to minimize sphere cage pluggage.
- Replaced the spheres in Module S-1 with three perforated stainless steel trays.

8.1.1 Forced Oxidation

Figure 8-1 summarizes the hours of boiler and module operation for the baseline test period (January 10 to February 10, 1981), and for the test period with adipic acid additions (February 10 to April 23, 1981). As this figure indicates, Module S-1 operated 61 percent of the time the boiler was on line during the baseline test period. Module S-2 operated 75 percent of the time during the baseline test period. During the adipic testing, Module S-1 operated 67 percent of the time while Module S-2 operated 69 percent of the time. The continuous monitoring system was 100 percent reliable during the baseline period and 77 percent reliable during the adipic test period. SO_2 monitors alone operated all of the time called upon during baseline testing and with 86 percent reliability during the adipic acid test period. Much of the scrubber downtime during the adipic acid testing occurred in February as a result of damage due to freezing. However, as Figure 8-2 shows, scrubber reliability was excellent for the last two months of forced oxidation testing.

For the 36-day period from March 10 through April 14, Module S-1 was available for all but 10 hours and Module S-2 for all but 7 hours. This represented the best availability the FGD system at SWPP had achieved up to that time. Credit for the notable increases in reliability should be given to the combination of overall system improvements in both the mechanics and operation of the scrubbers, as well as the addition of adipic acid. However, operation with adipic acid in the forced oxidation mode at fairly low pH values (high limestone utilization) reduced the chances for calcium solids dissolution in the mist eliminator and TCA cages. Thus, adipic acid additions contributed significantly to the higher scrubber system reliability.

Throughout the test period the condition of the major equipment which made up the FGD system was monitored so that the impact of individual equipment failure on the overall systems availability and performance (especially with respect to SO_2 removal), could be documented. Over the test period there were several equipment failures and malfunctions which limited the

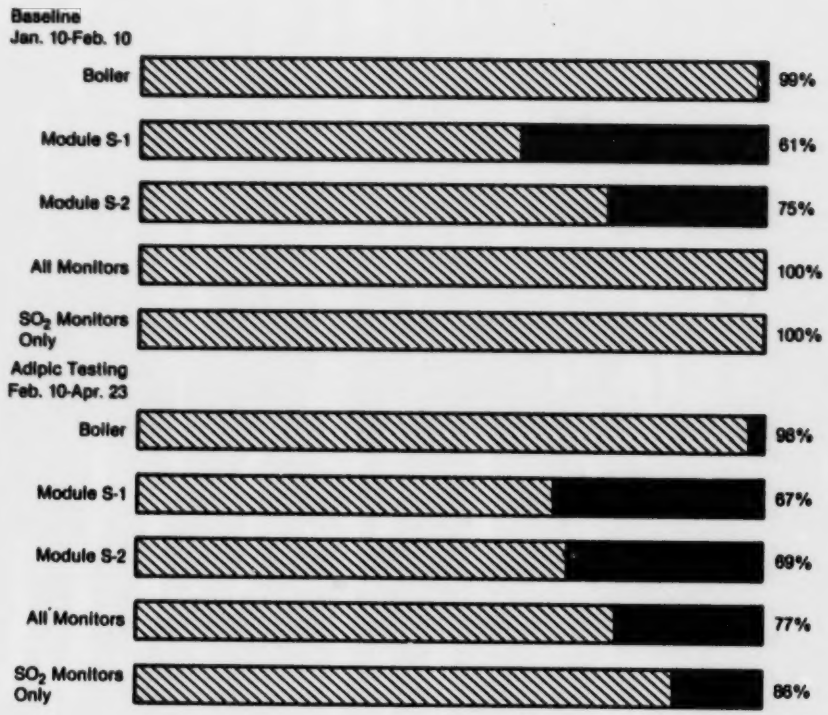


Figure 8-1. Boiler, Scrubber, and Continuous Monitor Reliability During Forced Oxidation Testing.

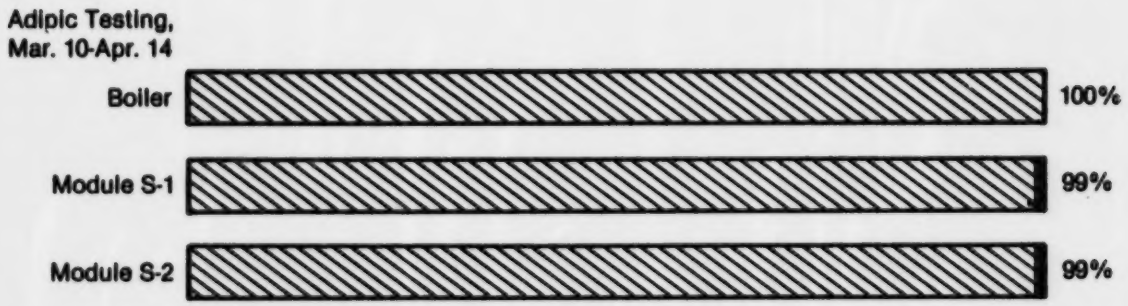


Figure 8-2. Boiler and Scrubber Reliability During March and April (Adipic Acid Testing).

systems's availability. The following failures/malfunctions accounted for virtually all of the downtime for Module S-1 over the baseline test period:

- A high temperature excursion inside the tower which melted most of the plastic spheres,
- Failure of the expansion joint between the A-ID fan and the scrubber module, and
- A failure in a water line feeding the module.

Over the adipic acid test period the following problems were responsible for over 90 percent of Module S-1 downtime:

- Freeze damage to the limestone feed lines, the supernatant return line from dewatering, and the mist eliminator pump and pump suction line,
- Pluggage in the thickener due to sulfate solids,
- Loss of agitator in limestone storage tank, and
- A high temperature excursion resulting in melting of the spheres.

Most of the downtime for Module S-2 during the baseline testing (January 10 to February 10) was due to a high temperature excursion which damaged its sphere charge. In addition, due to flue gas leaking past the isolation dampers, the module had to be taken off-line several times over a one-week period to allow maintenance crews to enter S-1 for repair work. During the adipic testing the following problems accounted for most of the forced outages in Module S-2:

- Freeze damage to return lines from dewatering, mist eliminator pump and pump suction line,
- Repair of damage to first level TCA cage and the screen and support braces in the presaturator area,
- Damaged limestone feeder belt,

- Pluggage in the thickener due to sulfate solids, and
- Loss of the agitator in the limestone storage tank.

The DuPont SO_2 monitors and Thermox O_2 analyzers were available during all of the baseline testing. However, some downtime was experienced during the adipic acid testing. It should be noted that neither the DuPont or Thermox analyzers were new purchases for this program. Both instruments are approximately ten years old and better reliability might be expected with state-of-the-art instrumentation. Major causes of continuous monitor failures included:

- Coil failure in ratchet relay which activiates the switching valve in sampling stations to alternate between S-1 and S-2 modules,
- Electrical short in the inlet Thermox O_2 analyzer,
- Aspirator pluggage and open drain valve on outlet sampling station, and
- DuPont coarse zero malfunction.

8.1.2 Natural Oxidation

Figure 8-3 shows the boiler, scrubber, and continuous monitor reliability for the baseline and adipic acid addition testing phases. As shown, the boiler was operated essentially all of the time during the natural oxidation test period (May 20 to August 31). Modules S-1 and S-2 were 95 and 84 percent reliable during the baseline testing (May 20 to June 12). The continuous monitoring system was available only 50 percent of the time required, while the SO_2 monitors were 99.8 percent reliable. The Thermox cell was found to be cracked during baseline testing, reducing the reliability of the overall monitoring system significantly.

During the adipic acid testing (June 24 to August 31), Modules S-1 and S-2 were 93 and 88 percent reliable, respectively. The continuous monitoring system was 95 percent reliable (as were the SO_2 monitors).

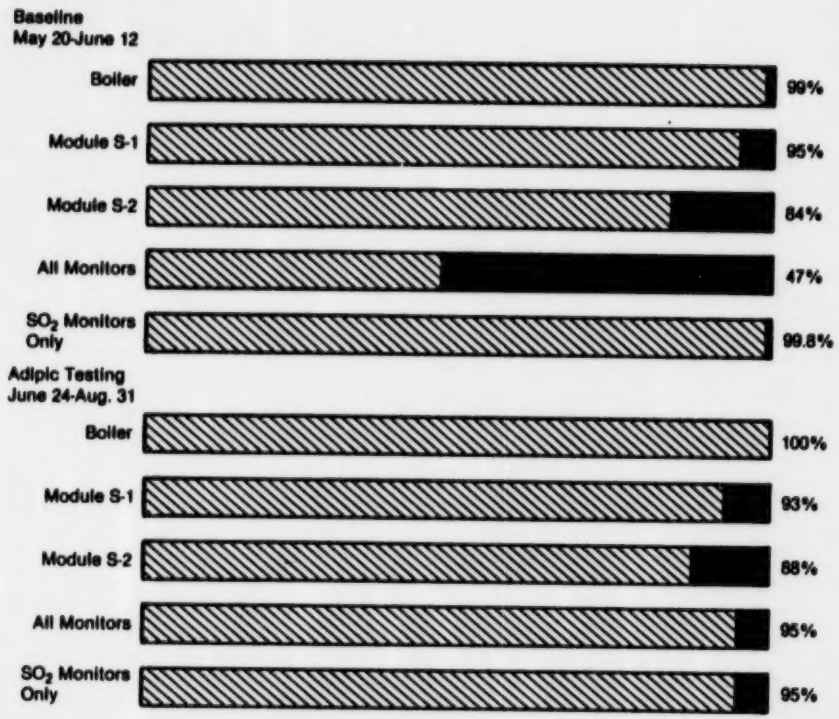


Figure 8-3. Boiler, Scrubber, and Continuous Monitor Reliability During National Oxidation Testing.

Module S-1 was operated during most of the three week baseline testing period. The only significant outages were caused by lightning damage to the supernatant tank level controller and a programmer controller power supply failure.

S-1 showed good reliability during the adipic acid testing. A modification to the scrubber trays resulted in a short outage. Lightning damage to the limestone supply equipment also brought down the scrubber for several days. Most of the forced outages for S-1 can be accounted for by the following problems:

- Lightning damage to the limestone supply equipment,
- Scrubber tray modifications,
- A leak in the slurry drawoff line from the scrubbers to dewatering,
- A damaged conveyor in dewatering, and
- Solids carryover from the thickener to the supernatant tank.

Module S-2's reliability (84 percent) during the baseline period was somewhat lower than that achieved by Module S-1 (95 percent). Forced outages during the baseline testing for S-2 were caused by:

- Lightning damage to the supernatant tank level controller,
- A presaturator line leak, and
- High thickener rake torque which forced one of the modules (S-2 was selected) off-line.

S-2 was slightly more reliable during the adipic testing (88 percent) than it was during baseline testing (84 percent). However, it was still less reliable than Module S-1. During the adipic acid test phase, S-2 was brought off-line to clean the TCA cages (which were plugged with slurry and ruptured TCA spheres) and to replace damaged TCA spheres. The sphere damage

was caused by failure to effectively isolate the module from hot flue gas when S-2 was off-line. The damaged spheres filled with slurry and sank to the bottom of the TCA cages, contributing to the pluggage problem. Major problems which led to forced outages of Module S-2 during adipic acid testing included:

- Lightning damage to the limestone supply equipment,
- A short outage to modify the trays in Module S-1,
- Damaged TCA spheres and pluggage of TCA cages,
- Solids carryover in the thickener, and
- A damaged conveyor at dewatering.

Numerous small problems arose with the continuous monitoring system during the natural oxidaton testing. The most notable of these was a broken Thermox O_2 sample cell at the inlet sample station which resulted in 12½ days of downtime for that monitor during June. Overall, however, the monitors achieved an 82 percent reliability, with the SO_2 monitors available 96 percent of the time required for service. Problems which led to monitor outages were:

- A broken inlet Thermox O_2 analyzer sample cell,
- Severe weather which knocked out the power supply to the instruments and shorted out one section of sample line heat tracing,
- Electrical problems in both the DuPont SO_2 analyzer sampling and control stations,
- Failure of the cam-drive motor in the DuPont control station,
- Failure of a valve in the inlet DuPont station to switch between S-1 and S-2 sample lines upon command of the control station, and
- A coil failure in the ratchet relay (which signals sampling stations to switch between S-1 and S-2).

8.1.3 DBA Testing

The DBA test phase ran from September 7 to October 7, 1981. The boiler was operated for the entire 744 hours in this period as shown in Figure 8-4. Module S-1 was operated 98 percent of the time required, and S-2 was 89 percent reliable. All monitors were operational 97 percent of the time required while the SO_2 monitors alone were operated all but one hour.

Module S-1 was operated 98 percent of the time it was called upon for service. High reliability of S-1 is somewhat deceiving, however, since it was required to operate only 659 of the total 744 hours of boiler operation. S-1 was not available for 95 hours during this period. However, S-1 was only required for service during 10 of the 95 hours it was not available. During the remainder of the time, the unit load was low enough that S-2 was able to handle all of the flue gas.

Most of the time when S-1 was not available can be attributed to mist eliminator pluggage. Plugged wash water nozzles prevented efficient cleaning of the mist eliminator blades. All of the downtime for S-1 during DBA testing can be accounted for by the following:

- Plugged mist eliminator wash water nozzles,
- Plugged lower mist eliminator,
- Solids carryover in the thickener overflow, and
- Presaturator spray nozzle repair.

Module S-2 was 89 percent reliable during the DBA test period. Like S-1, plugged mist eliminator wash water nozzles and a plugged mist eliminator contributed significantly to S-2's downtime. The majority of the downtime, however, was caused by a high thickener rake torque reading and a faulty recycle pump. (The high rake torque was caused by the solids inventory in the thickener building to a high level which necessitated taking one module

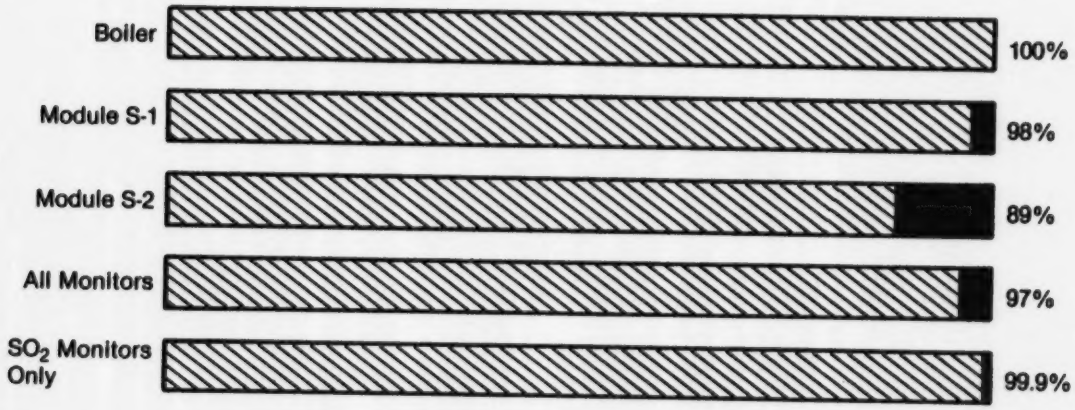


Figure 8-4. Boiler, Scrubber, and Continuous Monitor Reliability During DBA Testing.

offline until proper control could be re-established.) Another factor which lowered the reliability of S-2 compared to that of S-1 is that S-2 was required for 691 hours of service, whereas S-1 was required for only 659 hours. Overall, all downtime associated with S-2 during DBA testing can be accounted for by the following:

- High thickener rake torque,
- Plugged mist eliminator wash water nozzles,
- Leak in the bottom of absorber tower,
- Faulty recycle pump,
- Solids carryover in the thickener overflow, and
- Presaturator spray nozzles repair.

The continuous monitors proved to be very reliable during the DBA testing. All monitors were available 97 percent of the time. A plugged aspirator in the outlet sampling station accounted for virtually all continuous monitor downtime. Sufficient flow was maintained through the DuPont SO_2 analyzer to measure SO_2 concentrations accurately despite the pluggage. However, low flows through the Thermox analyzer resulted in erroneous O_2 readings until the aspirator pluggage could be removed. The only period during which the SO_2 monitors (as well as the O_2 monitors) were not operational was the 1-hour period when the ratchet relay switch in the monitor control station was replaced.

8.2 EQUIPMENT LIMITATION AND MODIFICATION

Several equipment associated limitations as well as modifications greatly impacted the reliability of the FGD system during the adipic acid demonstration program. Many of the modifications resulted in major improvements in the FGD availability during the testing. Other limitations, most notably those associated with the forced oxidized operation, resulted in lost operating time and increased fugitive water losses. A summary of the equipment related

problems and modifications during the forced oxidation, natural oxidation, and DBA testing is presented in the following sections.

8.2.1 Forced Oxidation

Overall system performance was excellent during most of the forced oxidation testing. However, the air compressors, dewatering equipment, and other miscellaneous problems caused operating difficulties which had to be overcome before meaningful testing could be continued.

A number of problems with the air compressors restricted their availability to the point that generally only 2 or 3 of the 4 compressors were in use at any time. When the system is not fully oxidized the concentration of dissolved sulfite increases. Since there are not adequate sulfite seed crystals for precipitation, the sulfite precipitates on the limestone particles causing blinding. In forced oxidation testing, this phenomenon caused a rapid drop in pH values and a decrease in SO_2 removal efficiency. This blinding seems to be a particular problem at 90 to 95 percent oxidation levels. Blinding can be solved quickly by increasing the oxidation air rate. Unfortunately, with low compressor availability both modules could not be fully oxidized. Due to this limitation, Module S-2 was kept fully oxidized (99+ percent), leaving S-1 to be only partially oxidized (average of 75 percent). Blinding in both modules was avoided for about the last 3 weeks of forced oxidation.

Numerous problems were encountered with the sludge dewatering plant equipment during the testing. These problems were primarily the result of the faster settling calcium sulfate solids. The plant was designed for dewatering a slurry that was primarily calcium sulfite. Pluggage was routine at a number of points around the dewatering plant. Normally this required discharges of slurry from the system to clear the pluggage. At one time the pluggage was severe enough to merit taking the two scrubber modules off-line while draining and cleaning the thickener.

The high-temperature excursions that caused forced outages during the testing were the result of a loss of power to the pumps which supply the quench water to the presaturator. Without this water, hot flue gas (300°F, 149°C) enters the towers, melting the plastic balls. The emergency scrubber trip goes into effect when high temperatures are measured in the presaturator. However, the flue gas cannot be isolated from the towers instantaneously since the dampers normally require one or two minutes to close. A source of quench water was later piped to the presaturator from the plant fire-water system. This measure should eliminate quench-water supply problems in the future.

Maintaining consistent and accurate operation of the on-line plant pH meters was very difficult. Calibration was required every 24 hours at a minimum. Signal drift and erratic response were almost daily occurrences. Most of the problem appeared to be due to the wet environment on top of the reaction tanks where the instruments were located. There were significant quantities of air sparged into the reaction tanks for forced oxidation which escaped the top of the tanks saturated with water. Cold weather caused the moisture to condense on the pH instrumentation in spite of the weather protection enclosure. Several times both primary and backup pH electrodes malfunctioned. During these periods, manual readings made by Radian personnel were used to keep the module operating as close to the set point as possible. This problem became much less frequent as the weather warmed. Daily calibration of the meters was continued to minimize span drift.

Freeze damage to the piping around the FGD system was due to the ineffectiveness of heat tracing the original FRP piping. Much of this pipe has been replaced with rubber lined carbon steel pipe which was heat traced and insulated. As a result, only a small number of freeze failures were experienced through the winter months, and only one resulted in a major forced outage.

8.2.2 Natural Oxidation

During the May plant outage, three levels of stainless steel perforated trays were installed in the S-1 scrubber module and all TCA spheres and cages were removed. Module S-2 remained a turbulent contact absorber (TCA).

In mid-July, S-1 was further modified to increase the gas pressure drop and SO_2 removal efficiency. Prior to this time, the pressure drop of Module S-1 had been on the order of 5-6 inches (13-15 cm) H_2O at full load, as compared to approximately 10 inches (25 cm) H_2O in S-2. SO_2 removal efficiencies were running lower in S-1 than in S-2 under similar operating conditions because of this difference in pressure drop. On July 18, the top two trays were partially blocked off by eight stainless steel strips. This increased the pressure drop in S-1 to 10-12 inches (25-30 cm) H_2O and the SO_2 removal efficiency to approximately that of S-2.

The other major modification which occurred during the natural oxidation test period was the installation of flow-through pH electrodes on both modules. Previously, dip-type electrodes had been used to monitor pH and control the limestone addition rate. The flow-through probes proved to be a constant problem throughout the summer testing. High slurry flows across the electrode resulted in a broken probe every two to three days. Too low a flow rate resulted in a plugged slurry feed line to the electrode and erroneous pH readings. In addition, significant drift occurred in the pH span despite daily calibration. Over 50 of the one hundred pH calibration measurements disagreed with the scrubber pH meter by greater than 0.1 pH units. Nearly 30 percent of the readings were 0.2 pH units or greater in error. The average difference between the span value used for calibration and the plant pH meter reading was 0.16 pH units.

Other modifications to the FGD system include an increase in the sludge-to-ash ratio in the sludge disposal system to compensate for a lower ash coal and higher SO_2 removals. Outlet damper seal air fans were also moved

to the upper level of the scrubber modules to increase their effectiveness. Unfortunately, both scrubbers had to be taken off-line to accomplish this move. As a result, S-1 and S-2 could not be effectively isolated from the hot flue gas during outages and some TCA sphere damage occurred in S-2.

The major limitation during the natural oxidation testing proved to be the temporary adipic feed system. Although the sacks of adipic acid were reportedly weatherproof, moisture was apparently picked up during the summer months resulting in troublesome adipic acid clumps. In addition, the automatic feeder discharged directly into an open limestone sump between the two ball mills. This area was extremely humid and further contributed to the adipic acid clumping problem. As a result, the adipic feed system plugged frequently, particularly in the summer months. An adipic acid storage, handling, and feed system that kept the solid adipic acid from exposure to the weather and high moisture areas should reduce the pluggage problem.

Fugitive water losses in the dewatering facility proved to be a problem, although to a much lesser degree, than during the forced oxidation testing. Breakdowns in the dewatering system hampered filtering and several times resulted in discharges to the emergency pond due to high rake torque readings in the thickener. Filter cake wash water (supernatant water) was also lost frequently due to the inability of the filter belt wash water return pumps to handle all of the wash water. Although not a major problem, water was occasionally lost in the overflow from the supernatant tank. This overflow was usually caused by excess makeup water being added to the system through leaks in the makeup water control valves. Excessive pump seal water inleakage also resulted in process water being lost from the system via the supernatant overflow when only one module was operating.

8.2.3 DBA Testing

The major modification to the FGD system during DBA testing was the addition of a temporary DBA feed system. DBA was fed to the limestone sump between the ball mills from a 6700 gallon (25.5 m^3) storage tank. The

storage tank was refilled every 3 to 5 days with DBA, which arrived by truck. Gravity flow from the tank to the limestone sump provided a sufficient feed rate without the use of a pump. The flow rate was controlled with a pinch valve.

Crystallization of DBA in the feed line proved to be a problem when the temperature dropped below 70°F (21°C). A permanent feed system would have to keep the solution above 70°F (21°C) to avoid crystallization. At Springfield, the problem was solved by adding sufficient DBA during the day to maintain the tank pH during the night and then shutting off the feed system and draining the feed lines each night.

No other modifications were made during the DBA testing. Mist eliminator pluggage and the deterioration of Module S-2 continued to provide some mechanical limitations. The deterioration of S-2 proved to be a problem since DBA feed to each module could not be controlled separately. Therefore, the DBA concentration in S-2 could not be raised to achieve the desired SO_2 removal without affecting the removal efficiency in S-1. Initial DBA usage was also increased due to the failure of one of the supernatant water return pumps which caused the supernatant tank to overflow. Overall, however, equipment related problems were not a signficant factor during the DBA testing, as reflected in the high scrubber reliabilities.

8.3 PHYSICAL EXAMINATION OF SCRUBBERS

Each of the scrubbers were examined whenever possible during the test program. This section describes briefly the condition of each of the scrubbers during the forced oxidation, natural oxidation, and DBA test periods. The primary reasons for conducting physical examinations of the scrubber were to: (1) detect any scale buildup or pluggage in the TCA sphere cages or on the trays; (2) determine the status of mist eliminator pluggage; (3) check the distribution of the TCA spheres; and (4) detect any corrosion or other damage to the scrubber internals.

8.3.1 Forced Oxidation

Very little scaling was noticed during the January to April forced oxidation period. The only location within either tower where any scale formation was noticed was on the mist eliminators. This occurred primarily on the upper mist eliminators in each module which were not washed. Scale formation was minor and occurred only in isolated areas during forced oxidation testing. Operation at lower pH values and at high SO_2 removals helped reduce mist eliminator scale formation.

Pluggage of the TCA sphere cages has historically been a recurring maintenance problem at SWPP. This problem was closley watched during testing but only a few cages showed signs of pluggage after extended runs. The lack of pluggage experienced during the tests are probably due to: (1) the high loads the system routinely operated at (promoting good turbulence in the cages); (2) reduced ball charges (approximately 12 inches (30 cm) total height); (3) high limestone utilization; and (4) decreased scaling potential due to the presence of calcium sulfate during forced oxidation testing.

Nozzle damage in the modules was primarily restricted to the presaturator spray nozzles. Most of the nozzles which were made of Carpenter 20 had corrosion damage, and in several instances the piping up to the nozzle had corroded away. Improvements in nozzle life had been gained as a result of a piping change made during the fall 1980 outage. The change resulted in supplying clear liquor to the nozzles instead of solids-laden mist eliminator wash water. This step eliminated errosion damage as well as solids pluggage of these nozzles. No noticeable damage to the ceramic scrubber feed recycle nozzles occurred. Several of the nozzles in each module had plugged either partially or completely with pieces of rubber liner and plastic balls, but this problem was not widespread.

Module S-1 was taken out of service on April 15 due to ball damage caused by a high-temperature excursion. This module was then cleaned out and prepared for conversion to a tray tower. Examination of Module S-2 at the conclusion of the forced oxidation study (April 23) showed its TCA spheres to be in relatively good condition. In some cases, doors on the TCA cages had come loose resulting in migration of the TCA spheres. Overall, however, both modules seemed to be in very good condition following the forced oxidation testing.

8.3.2 Natural Oxidation

Module S-1 appeared to be in good condition throughout the natural oxidation testing. Blocking off parts of the top two trays did not seem to cause any problems. Some scale was noted on the lower tray after about 2½ months of operation. However, this was removed with relative ease and did not result in pluggage of any of the tray holes. The mist eliminator also showed some scale buildup by the end of the testing. Mist eliminator scaling was probably due to several factors. SO_2 removal efficiencies were in general lower and limestone stoichiometries and pH set point were often higher during the natural oxidation testing than during the forced oxidation study. Lower removals in the absorber section increase the SO_2 driving force for removal in the mist eliminators (since more SO_2 was present in the exit gas). Higher stoichiometries mean more $CaCO_3$ is present in the slurry carried up to the mist eliminators (where it dissolves). Thus, increased SO_2 removal in the mist eliminator (some of which is oxidized to $SO_4^{=}$) along with higher dissolved calcium values will tend to raise the Ca^{++} and $SO_4^{=}$ levels in the mist eliminator wash water and increase the risk of $CaSO_4 \cdot 2H_2O$ scaling. Another factor which probably contributed to the increased scale is that the mist eliminators were not cleaned after the forced oxidation testing. Therefore, some of the increased scale was probably due to crystal growth of $CaSO_4 \cdot 2H_2O$ on the existing crystals. Finally, the most significant cause of increased mist eliminator scaling is the failure to wash the upper mist eliminator section. In most cases, scale formation was minimal in mist eliminator sections that were washed.

Module S-2 experienced essentially the same problems with mist eliminator scaling as did S-1. Again, this scaling was not severe. However, there was a noticeable increase over the amount found during forced oxidation. The most severe problem noted in S-2 was the pluggage of several TCA cages and the failure of TCA spheres. An examination of S-2 on August 15 showed ten of the thirty cages to be completely or partially empty. Damaged TCA spheres were observed in virtually all of the cages which contained spheres and approximately 30 percent of the cages were found to be partially or completely plugged with limestone slurry. This had a marked effect on the SO_2 removal efficiency of Module S-2 (which was approximately 5 to 10 percent less than the removal efficiency achieved by S-1 under similar operating conditions).

Deterioration of the S-2 module was caused by the natural attrition of the TCA spheres (historically a problem at SWPP) and the exposure of the module to hot flue gas when S-2 was taken off-line during the natural oxidation testing. Infiltration of hot flue gas was more of a problem during the early phases of natural oxidation testing than it was during normal operation due to the lack of seal air on the scrubber outlet isolation dampers. Outlet seal air fans were moved to the top of the scrubbers during the natural oxidation testing. During the process of moving the seal air fans, however, seal air was not available.

8.3.3 DBA Testing

The performance of S-2 was improved for a time after the module was recharged with the remainder of Southwest's replacement TCA spheres on August 15. Unfortuantely, there was not enought time during the August 15 physical examination (performed during a scheduled load reduction when S-2 was not required for service) to thoroughly clean the TCA cages and replace all of the damaged spheres. The purchase of additional replacement spheres for S-2 could not be justified since it was scheduled to be converted to a tray tower during the October plant outage. As a result, the performance of S-2 deteriorated again fairly rapidly. This deterioration was reflected in the Modules SO_2

removal performance during DBA testing. At the conclusion of the DBA test period, 9 of the 30 TCA cages were plugged and 5 were empty.

The lower mist eliminator wash nozzles were plugged completely following a dewatering upset caused by insufficient flocculent feed. This upset resulted in solids overflowing the thickener and being returned to the scrubber with the recycled thickener supernatant. The upset was partially due to a high unit load-high SO_2 removal period which resulted in a very large quantity of sludge discharged from the scrubbers to the thickener. The increased mass flow of solids was not accompanied with an increase in flocculent feed. Module S-2 was taken off-line after a few days of operating without mist eliminator sprays and both the upper and lower banks had scaled significantly during this short period of time. Module S-1 was not taken down to unplug its mist eliminator wash nozzles for several more days, and by then scaling of the banks had all but plugged them. A three-day outage was requred to unplug the mist eliminators so the module could be put back in service.

The upper two trays in S-1 were clean; however, scale buildup was noticed on the lower tray. Again, this was cleaned with relative ease. In summary, conditions such as cage pluggage and mist eliminator scale formation continued during the DBA testing. No new problems associated solely with the DBA test period were noticed.

SECTION 9

COST ANALYSIS OF OPTIONS TO IMPROVE SWPP SCRUBBER SO_2 REMOVAL EFFICIENCY

Information gathered on the performance of the SWPP scrubbers during baseline testing showed that they were incapable of maintaining the unit in compliance with the existing SO_2 standard (1.2 lbs SO_2 per 10^6 Btu heat input) in their existing configuration. A study was conducted to aid City Utilities in evaluating the options for improving the scrubbers' SO_2 removal efficiency. Four options were examined which could improve removal efficiency. These were:

Option 1 - Increase scrubber slurry recycle rate

Option 2 - Add adipic acid

Option 3 - Add DBA

Option 4 - Convert the two modules to spray towers and increase slurry recycle rate

The objective of the study was to evaluate the four options primarily on a cost basis. However, each option was also examined with respect to its technical merits. Several times during the course of the test program both recycle pumps on a module were operated simultaneously for short periods and the results were documented. These short tests showed significant improvements in SO_2 removal efficiencies. However, during one hour-long test there was a drop in reaction tank level equivalent to over 10 percent of its volume. Slurry had evidently been entrained in the flue gas then removed in the mist eliminators and routed from the mist eliminator wash trap-out trays to the thickener, bypassing the reaction tank. This operating problem would need further investigation before Option 1 could be considered viable.

Options 2 and 3 were investigated thoroughly during the test program. Conditions were specifically controlled during the adipic acid natural oxidation testing and DBA testing to simulate the operation of the scrubbers at the SWPP compliance SO_2 removal level (approximately 85 percent). Required buffer feed rates were calculated from material balances for these tests. Operating problems were identified and solutions determined during the tests.

Option 4 could not be tested at SWPP because of the significant modifications that it would require. Based on past experiences and the SWPP tower designs, this options's technical merits were evaluated. At high unit loads, the gas velocity through each tower could routinely reach 13 feet per second (3.9 meter/second). This velocity is above normal design values for spray towers and could lead to gas/slurry entrainment problems.

An important consideration in the evaluation of the options was the effect that limestone classifiers would have on the costs. By the summer of 1982, City Utilities was planning to install classifiers on the limestone ball mills to control their fineness of grind. According to pilot and prototype data, the finer limestone grind should improve SO_2 removal efficiencies. With higher SO_2 removals, less adipic or DBA would be needed for Options 2 and 3, and the increase in recycle rate would not have to be as large for Option 1. Taking credit for the advantages of the installation of the classifiers gave costs for what was identified as Options 1A, 2A, and 3A. Option 4 was not evaluated with the credit because of its technical uncertainty.

A present worth (or cost) analysis was used for evaluating the economics of the different options. With this method, all project expenditures (capital and operating) are discounted back to year one using a discount factor which was assumed for this study to be equal to the general inflation rate. All capital costs were assumed to be spent in year one of the study (1982) for the buffer additive options (2, 3, 2A, and 3A) while capital costs for Options 1, 1A, and 4 was assumed to be spent over the first two years since City

Utilities anticipated that these projects would be financed in this manner. The general inflation rate and operating and maintenance escalation rates were selected to be consistent with City Utilities' long-term planning basis.

The projects were evaluated over a fifteen year life. The present cost of each option for each year over the fifteen year period was then calculated taking into account the escalation rates. To compare the costs, the cumulative yearly present costs were calculated and then plotted over the life of the option. The results are shown in Figure 9-1 for Options 1, 2, 3, and 4 and in Figure 9-2 for Options 1A, 2A, and 3A. In both figures the DBA option represents the least cost alternative, despite the fact that it must be fed at a rate approximately 33 percent higher than for adipic acid. This difference is more than made up for in the lower delivered cost of 30¢ per lb (67¢/kg) for DBA versus 59.5¢ per lb ($1.33/kg) for adipic acid. Increasing the slurry recycle rate is more expensive than aidpic acid addition for the first nine years when comparing the options which take credit for the classifiers. Beyond nine years, though, the lower operating costs for increasing the recycle rate makes this option cheaper. Even at the end of fifteen years, though, the DBA option is some $300,000 less expensive on an present worth basis than is the increased recycle rate option.

A more detailed presentation of the cost analysis is included in Appendix B.

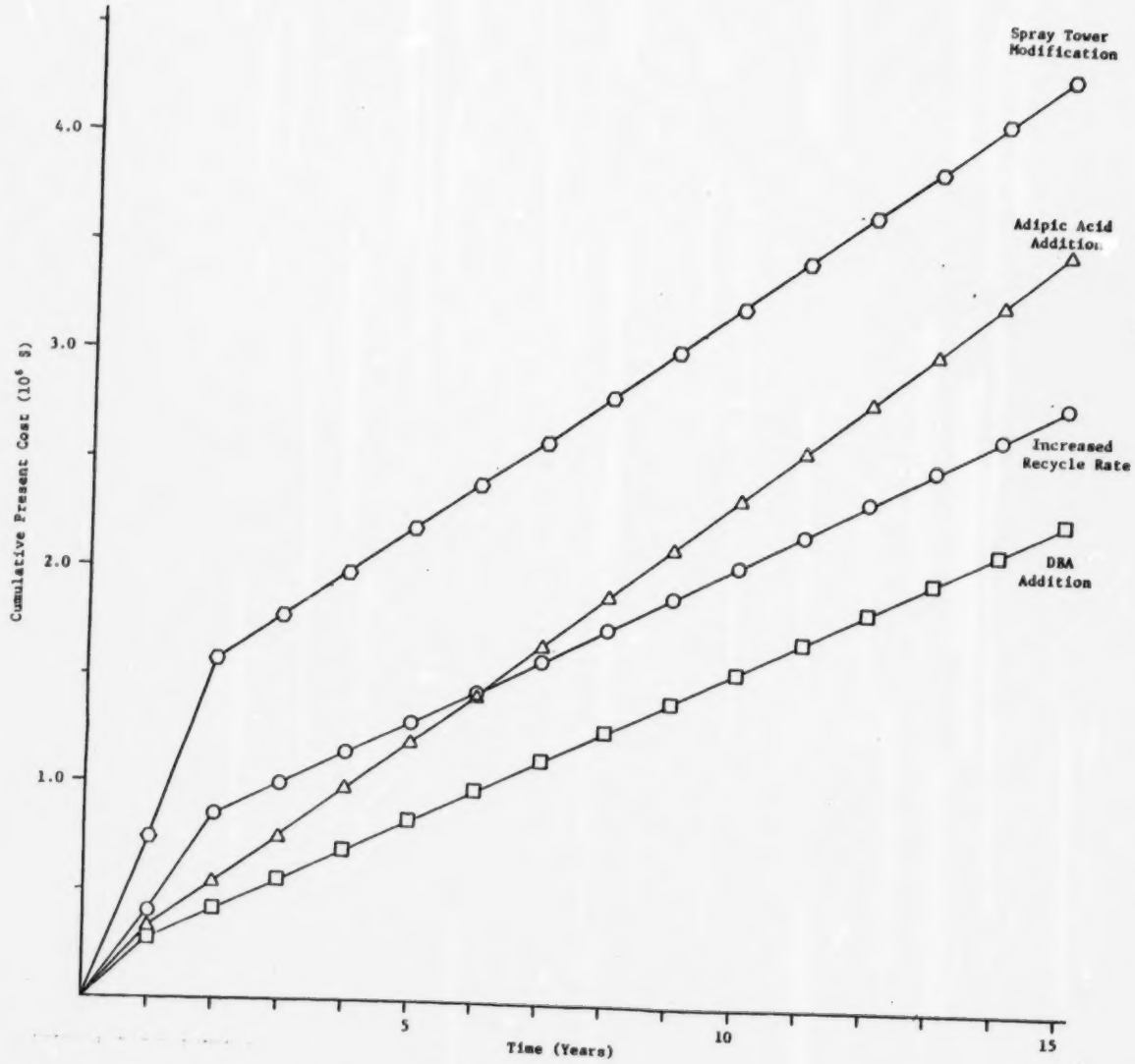


Figure 9-1. Cumulative present cost for options 1, 2, 3, and 4.

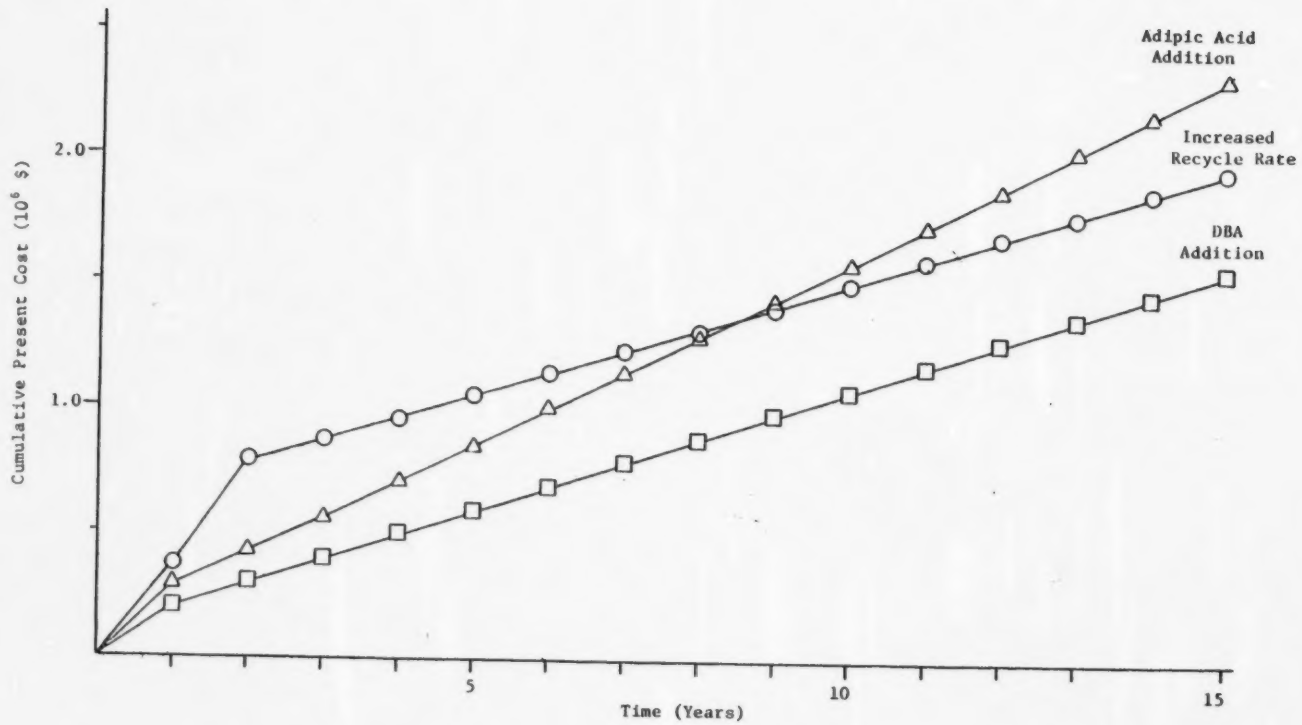


Figure 9-2. Cumulative present cost for options 1A, 2A, and 3A.

SECTION 10

SOLID WASTE TESTING

This section discusses the test results obtained on samples of various solids wastes generated during the demonstration program. Four samples were tested for: (1) H_2S generation by fermentation; (2) bioassay results including cytotoxicity, mutagenicity, acute toxicity; and (3) RCRA and ASTM leaching extraction. A sample from each of the operating conditions was selected for these tests. Both natural and forced oxidation solids with adipic acid, and natural oxidation with dibasic acid (DBA) were selected for analysis. The base case sample was natural oxidation solids without any organic acid additive. All of the samples were mixed with fly ash from Springfield. This was done in order to examine a "worst case sludge" due to the effects of trace elements in the fly ash. Small amounts of river bank soil (<1 percent) were added to the samples as a source of bacteria for the fermentation tests. The results of each type of analysis are discussed in the following sections.

10.1 FERMENTATION

Solids samples were mixed with deionized water to produce a 50 weight percent slurry and placed in 500 ml brown glass jars. The bottles were approximately one-half full and the air space was purged with nitrogen before the bottle was sealed. The objective of the fermentation tests was to determine the magnitude of H_2S and CO_2-CH_4 generation under anaerobic conditions. This test was designed to simulate conditions at the bottom of a sludge pond. The sample bottles were continually agitated over a two-month period in temperature controlled chamber (35°C). At the end of this period, the pressure in each bottle was measured with a water manometer. The bottles were sniffed to qualitatively determine if H_2S was present (typical threshold limit - 1 ppm)

Table 10-1 presents the compositions of the solids tested and the results observed. In each sample, FGD solids and fly ash were present in roughly equal amounts. Solids from the pug mill at Springfield were used as sample material. Soil, bacteria (desulfovibro desulfuricans) and nutrient (sodium lactate) were added in small amounts to various samples in an attempt to generate H_2S. Only under one set of conditions (with bacteria and nutrients) was H_2S detected. No significant pressure change was noted in any of the samples. The absence of H_2S formation and pressure build up indicates that anaerobic decomposition of FGD sludge, with or without carboxylic acids present, is minimal.

It was initially planned to test the fermented solids of sample number 3 for biological effects and leachates. However, since no H_2S was generated by fermentation, these solids were judged to not be significantly different from the unfermented solids so further tests of this sample were not performed.

10.2 BIOASSAY TESTS

Level 1 bioassay tests were conducted on four solid samples, identified in Table 10-2. The mutagenicity and cytotoxic evaluations were performed by Litton Bionetics while the aquatic invertebrate test was done by Battelle Laboratories. Each test procedure and the results are discussed further below.

TABLE 10-2. LEVEL 1 BIOASSAY SAMPLES

Sample	Composition
1	Natural oxidation, fly ash, soil
2	Natural oxidation, fly ash, soil, adipic acid
4	Forced oxidation, fly ash, soil, adipic acid
5	Natural oxidation, fly ash, soil, dibasic acid

TABLE 10-1. FERMENTATION TEST CONDITIONS AND RESULTS

Sample	FGD Solids Oxidation	Fly Ash	Organic Acid	Soil	Bacteria	Nutrient	H_2S
1	Natural	Yes	No	Yes	No	No	No
2	Natural	Yes	Adipic	No	No Yes	No 1.0 ml 10.0 ml	No
3	Natural	Yes	Adipic	Yes	No Yes	No	No
4	Forced	Yes	Adipic	Yes No	No Yes	No 1.0 ml 10.0 ml	No Yes
5	Natural	Yes	DBA	Yes	No Yes	No 1.0 ml 10.0 ml	No
6	Natural	No	No	No	Yes	No 1.0 ml 10.0 ml	No

Sample 3 was to have been a fermented sample of the sample 2 solids. However, as discussed in the previous section, the fermentation results were negative. Consequently, this sample was not analyzed. Appendices E, F, and G contain the full reports of the Litton and Battelle test work. Table 10-3 summarizes the results of the boiassay tests.

As can bee seen in Table 10-3, only the freshwater invertebrate test showed low to high toxicity levels in all samples. The high pH (10.5-11.1) observed in all but sample #4 was likely the major contributor to the observed toxicity since pH greater than approximately 9 adversely effects Daphnia magna. This conclusion is further corroborated by the fact that the higher the pH, the greater the toxicity. A low level of toxicity was observed in sample #4, where pH was well within the normal tolerence range for Daphnia, indicating some other causal agent. The analytical chemistry data (see Table 10-6) showed no potentially toxic constitutents present in significant quantities leaving the relatively high TDS as the most likely cause in this sample. Since the chemistry for the other three samples are similar (except for pH), it may be concluded that TDS is also contributing in part to their toxicity. It is apparent that Daphnia is the most sensitive of the bioassays used and the only one showing toxicity. The toxicity observed is due essentially to pH and TDS rather than the presence in significant quantities, of a particular hazardous compound. Overall, the available toxicity and chemistry data indicate that these four samples do not constitute a significant environmental hazard.

The overall conclusion that can be made from the data is that organic buffers containing sludges are not significantly different from sludge without buffers from a Level 1 toxicity standpoint.

10.2.1 Mutagenicity Evaluation

The Ames Salmonella/microsome mutagenesis assay has been shown to be a sensitive method for detecting mutagenic activity for a variety of chemicals representing various chemical clases [20]. This assay is one of several recommended by EPA to identify, categorize and rank the pollutant potential of influent and effluent streams from industrial and energy-producing processes. This assay has been well validated with a wide range of positive and negative control chemicals and complex environmental samples.

TABLE 10-3. BIOASSAY RESULTS SUMMARY

Sample	Ames Salmonella		CHO Cytotoxicity		Fresh Water Invertebrate	
	Solid	Leachate	Solid	Leachate	Solid	Leachate
1-Natural oxidation, fly ash, soil	ND	ND	ND	ND	NT	M
2-Natural Oxidation, fly ash, adipic, soil	ND	ND	ND	ND	NT	H
4-Forced Oxidation, fly ash, adipic, soil	ND	ND	ND	ND	NT	M/L
5-Natural Oxidation, fly ash, DBA, soil	ND	ND	ND	L/ND	NT	M

NT - No test performed

ND - No detectable toxicity or mutagenicity

L - Low toxicity

M - Medium toxicity

H - High toxicity

The four samples, FGD sludge Samples #1, 2, 4, and 5 were leached in sterile deionized water. Thirty grams of each sample were added to 120 ml of sterile deionized water and shaken for 48 hours at 200 rpm. After incubation, the leachate was decanted and remaining solids were removed by centrifugation. The supernatant was then fiter sterilized by passing the liquid through a 0.45μ filter. The resulting leachate and the unextracted solid were tested for their genetic activity in the EPA Level Ames Salmonella assay in the presence and absence of a metabolic activation system.

The solid samples were assayed at a single concentration of 5.0 mg per plate and the leachates were assayed at four concentrations of 10, 50, 100 and 200 μl per plate.

Solvent control and positive control values were within acceptable ranges. These results achieved assay acceptance criteria and provided confidence in the assumptions that the recorded data represented typical responses to the test material.

Sample #1 (Natural oxidation, fly ash, soil)--

The results of the assays conducted on Sample #1 before extracting in water were negative in the presence and absence of a metabolic activation system. The minimum effective concentration (MEC) was greater than 5 mg/plate which permitted the sample to be ranked as having nondetectable (ND) mutagenic activity.

The results of the assays conducted on Sample #1 leachate were also negative both in the activation and nonactivation assays. The sample was evaluated as having nondetectable (ND) mutagenic activity based upon a MEC greater than 200 μl/ml.

Sample #2 (Natural oxidation, fly ash, soil, adipic acid)--

The results of the assays conducted on the solid as well as aqueous leachate of sample #2 were negative in the presence and absence of a metabolic activation system. The test with the leachate was repeated with strains TA-98 and TA-100 in the presence of the metabolic activation system because of the low number of revertants observed at various test doses in the initial assay. These repeat tests were also negative.

Both forms of sample #2 were ranked as having nondetectable (ND) mutagenic activity. These evaluations were based upon MEC values greater than 5 mg/plate for the solid form and greater than 200 µl/plate for the aqueous leachate of the sample.

Sample #4 (Forced oxidation, fly ash, soil, adipic acid)--

The results of the assays conducted on the solid as well as aqueous leachate of sample #4 were negative in the activation and nonactivation assays. The strain TA-98 exhibited an increased number of revertants at the 200 µl/plate dose with the leachate but the increases were considered not significant since no dose-related response was observed. The test with the leachate was repeated with strains TA-1537 and TA-100 in the nonactivation assays because of the low number of revertants observed at various test doses in the initial assay. The repeat tests were also negative.

The mutagenic response of sample #4 was basically similar to that seen with samples #1 and #2. Both the solid form and the aqueous leachate of Sample #4 were ranked as having nondetectable (ND) mutagenic activity based upon MEC values greater than 5 mg/plate for the solid and 200 µl/plate for the leachate.

Sample #5 (Natural oxidation, fly ash, soil, dibasic acid)--

The results of the assays conducted on both the solid and the aqueous leachate of sample #5 were negative in the activation and nonactivation assays. The assays with the leachate were repeated with all the strains with both activation and nonactivation, since a few contaminating microbial colonies were observed on the test dose plates. These repeat tests performed on the leachate were all negative. Since no MEC values were observed, the two forms of sample #5 were ranked as having nondetectable (ND) mutagenic activity.

It must be emphasized that the Ames *Salmonella*/Microsome Plate Assay is not a definitive test for chemical carcinogens. It is recognized, however, that correlative and functional relations have been demonstrated between these two endpoints. The results of comparative tests on 300 chemicals by McCann *et al.*[21] show an extremely good correlation between results of microbial mutagenesis tests and *in vivo* rodent carcinogenesis assays.

10.2.2 Cytotoxic Evaluation

The Chinese hamster ovary (CHO) clonal toxicity assay has been shown to be a sensitive method for detecting cytotoxic activity for a variety of chemicals representing various chemical classes[20]. This assay is one of several recommended by EPA to identify, categorize and rank the pollutant potential of influent and effluent streams from industrial and energy-producing processes. This assay has been well validated with a wide range of positive and negative control chemicals and complex environmental samples.

The results of the CHO clonal toxicity assays are presented below. The calculated relative survival values were obtained by comparing the average number of colonies per dish for each of the assayed concentrations to the appropriate control value. The relative survival values were then plotted as functions of the applied concentration of test material per ml of culture medium. Curves were fitted to the data points by eye in order to determine the EC_{50} value for each sample and to rank each sample according to EPA Level 1 evaluation criteria.

Sample #1, (Natural oxidation, fly ash, soil)--

The test material in both the solid and aqueous leachate forms caused only small reductions in the colony forming ability of cultured CHO cells. The solid form of the sample produced a gradual reduction in cell survival over the range of concentrations tested (1 μg to 1000 μg/ml) and reduced the survival to about 60 percent at the maximum applicable dose (MAD) of 1000 μg/ml. Since the EC_{50} value was clearly greater than 1000 μg/ml, the sample was ranked as having nondetectable (ND) toxicity.

The aqueous leachate of sample #1 caused no toxicity between 10 μl and 100 μl/ml, but a gradually increasing toxicity was observed between 100 μl and 600 μl/ml. While some toxicity was observed in the low toxicity range (60 μl to 600 μl/ml), no concentration reduced the relative survival below 76 percent. The EC_{50} was greater than 600 μl/ml and the test material was ranked as having nondetectable (ND) toxicity.

The toxic response of CHO cells to both the solid and aqueous leachate forms of sample #2 was very similar to that observed for sample #1. Gradually increasing toxicity was caused by the solid form of the sample. Maximum toxicity was observed at the MDA of 1000 μg/ml and the survival was about 65 percent. The sample was therefore ranked as having nondetectable (ND) toxicity.

The aqueous leachate of sample #2 gave negligible toxicity below 100 μl/ml, and the toxicity increased only slightly as the concentration increased from 100 μl to 600 μl/ml. The survival at 600 μl/ml was about 81 percent; so the sample was ranked as having nondetectable (ND) toxicity.

Sample #4 (Forced oxidation, fly ash, soil, adipic acid)--

The solid form of sample #4 produced no increase in toxicity between 1 μg and 300 μg/ml. A very slight increase in toxicity was noted above 300 μg/ml, causing a reduction in survival to 85 percent at the MAD of 1000 μg/ml. Therfore, the EC_{50} was greater than 1000 μg/ml and the sample was ranked as having nondetectable (ND) toxicity.

The aqueous leachate of the sample caused a gradually increasing toxicity over the range of doses tested (10 μl to 600 μl/ml). The relative survival did not approach 50 percent and reached a minimum of 69.5 percent at the MAD of 600 μl/ml. The sample was ranked as having nondetectable (ND) toxicity.

Sample #5 (Natural oxidation, fly ash, soil, dibasic acid)--

Gradually increasing toxicity was observed for the solid form of sample #5 between 1 μg and 300 μg/ml. As occurred for the solid form of sample #4, an increase in toxicity was obtained at concentrations above 300 μg/ml. The relative survival did not fall below 66 percent (1000 μg/ml), so the EC_{50} was greater than 1000 μg/ml. Thus, the sample was ranked as having nondetectable (ND) toxicity.

The assay on the aqueous form of sample #5 was the only test in this series where an EC_{50} value was observed. The sample had negligible toxicity between 10 µl and 100 µl/ml, but the toxicity increased steadily from 100 µl to 600 µl/ml and reached a maximum corresponding to 45.9 percent relative survival at 600 µl/ml (Figure 10-1). The EC_{50} was estimated to be 545 µl/ml, a value in the low toxicity range but one which closely approached the low/nondetectable boundary of 600 µl/ml. Because of normal experimental variation, repeat trials could be expected to produce EC_{50} values at, or somewhat above, the low/nondetectable borderline. For this reason, the aqueous form of sample #5 was ranked as having low/nondetectable (L/ND) borderline toxicity.

The cells used for the eight assays were in logarithmic growth phase and were at least 97 percent viable (average value of 99.4±0.5 percent). Greater than 70 percent of the seeded cells formed colonies in the negative controls of each of the eight assays (77.6±6.7 percent). Colony growth was normal and well distributed on the culture dishes in all trials. The combined results were considered to achieve assay acceptance criteria and provided confidence in the assumption that the recorded data represented typical responses to the test materials.

The EC_{50} value represents the concentration of test material that reduces the colony-forming ability of CHO cells to 50 percent of the vehicle or negative control value. EC_{50} values are determined graphically by fitting a curve by eye through relative survival data plotted as a function of the logarithm of the applied concentration. Each data point normally represents the average of three culture dishes. In order to indicate the variability of the data, the high and low colony counts for each concentration are used to calculate the relative survivals, and the range is shown by a bar at the position of the plotted average. If no bar is shown, the variability was within the size of the symbol. Statistical analysis is unnecessary in most cases for evaluation.

The toxicity of the test material is evaluated as high, moderate, low, or nondetectable according to the range of EC_{50} values defined in the following table.

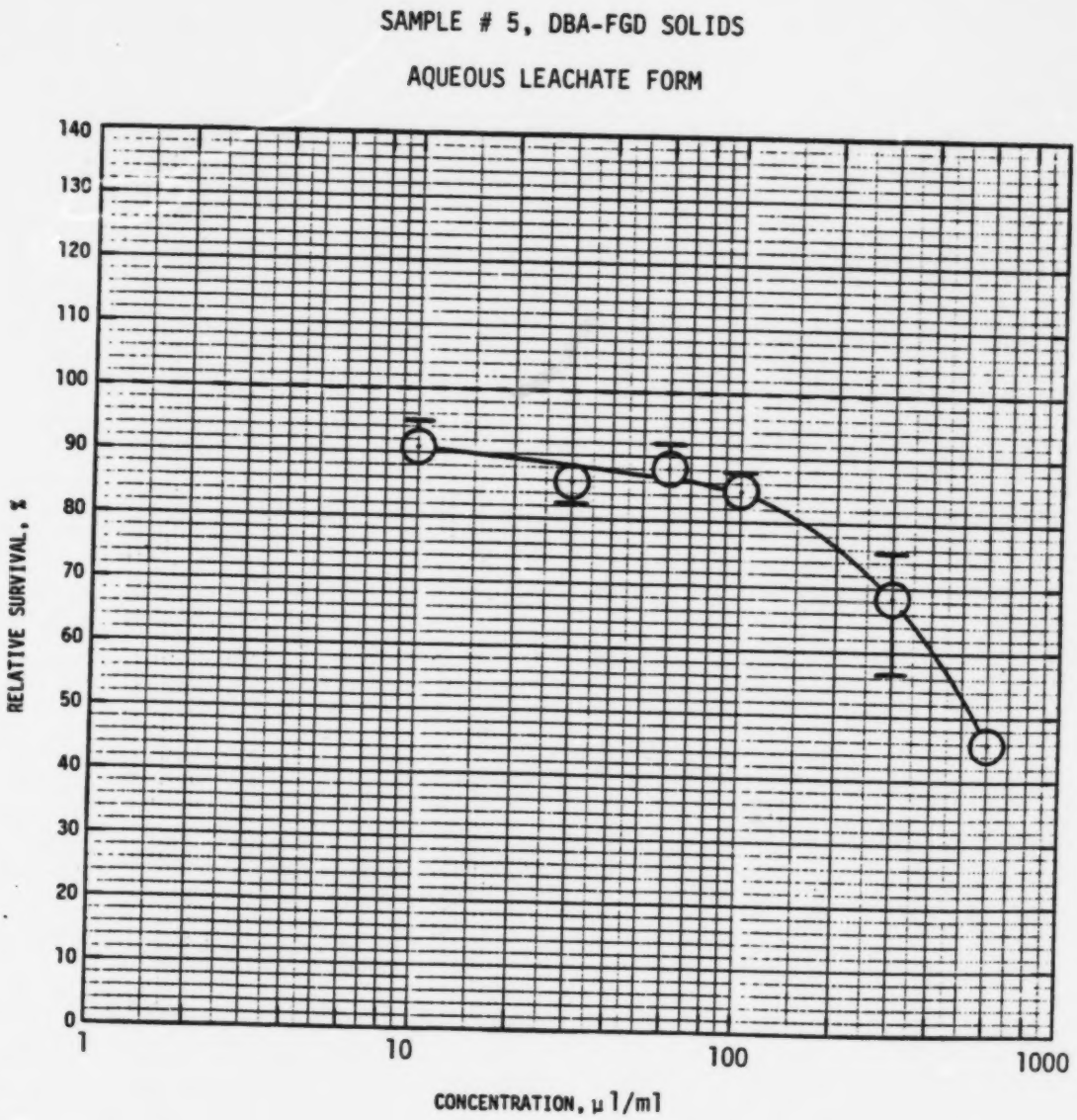


Figure 10-1. Rodent cell (CHO) clonal toxicity assay EC_{50} determination.

Toxicity[a]	Solids (EC_{50} in μg/ml)	Aqueous Liquids (EC_{50} in μl/ml)
High	<10	<6
Moderate	10 to 100	6 to 60
Low	100 to 1000	60 to 600
Not Detectable	>1000	>600

[a]Evaluation criteria formulated by Litton Bionetics, Inc. for IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests.

10.2.3 Acute Toxicity

Leachate was prepared from four solid samples for use in the fresh water invertebrate toxicity evaluation. A 20 percent slurry was formed and agitated for 48 hours. The liquid was then filtered through a 0.45μ filter. Solids samples were not tested in this evaluation.

EPA Level 1 procedures[22] were used in the biological testing. First instar *Daphnia magna* were used for static acute bioassays. All test organisms were taken from cultures originating from a single female to ensure uniformity of strain. Daphnids were cultured in dilution water at test conditions and selected during the log phase of growth of the culture.

The test consisted of six concentrations in a geometric series with each concentration being 50 percent of the previous concentration. (The maximum applicable dose is 100 percent of a liquid sample). Five organisms were used per replicate with three replicates per concentration and control. The tests were conducted at 19±2°C with a photoperiod of 16 hours light and 8 hours dark. Specific conductance was measured at the beginning of the test and dissolved oxygen, pH, and temperature were recorded initially and after 48 hours. Immobilization, defined as lack of movement except for minor activity of appendages, was the criterion for effect. Immobilization and abnormal behavior were recorded every 24 hours. Immobilized organisms were removed.

The EC_{50}, the concentration of test material which immobilized 50 percent of the Daphnia magna, and its 95 percent confidence limits were calculated for 24- and 48-hour exposures using probit analysis.

The probit method of data analysis uses the probit transformation and the maximum liklihood curve-fitting technique. This method assumes that the concentration-mortality curve is linear. Stephan[23] recommends the logarithmic transformation of concentration data to help assure this linearity. However, the analysis employed by Battelle uses the probit transformation both with and without the log transformation of the concentration data. The results are examined to ascertain which method gives the best fit to the probit curve. The appropriate EC_{50} is then reported.

The probit method of analysis also allows the calculation of 95 percent confidence limits about the EC_{50}. While the confidence limits do give information about the precision of the individual EC_{50} estimate they do not indicate the reproducibility or repeatability of acute mortality tests done at different times or in different laboratories[23].

All four FGD sludge samples were toxic to Daphnia magna as shown in Table 10-4. Survival at each test concentration in addition to the other parameters measured are tabulated in Appendix E.

Results indicate that two of the four FGD solids were moderately toxic to Daphnia according to the toxicity categories for aquatic ecological assays. Sample #2 was ranked highly toxic and Sample 4 had low to moderate toxicity.

The resulting patterns show that high pH was the major cause of toxicity in Samples 1, 2, and 5. The pH of the pure leachate at the outset of the test (see the last line in Table 10-6) was greater than 9 which is the approximate upper tolerance limit for Daphnia. Thus, at the higher test concentrations, pH was definitely a stressor. A review of the raw bioassay data for pure leachate in the Battelle report shows that in these three samples the pH dropped during the 48 hour test period. In Samples 1 and 5 the pH had dropped

TABLE 10-4. EC_{50} VALUES FOR DAPHNIA MAGNA OF FGD SLUDGE SOLIDS

Sample	24-Hour EC_{50}[a] Percent Concentration	48-Hour EC_{50}[a] Percent Concentration	Relative[b] Toxicity
1-Natural oxidation, fly ash, soil	73.3 (40.5-106.1)	44.9 (32.1-57.8)	Medium
2-Natural oxidation, fly ash, soil, adipic	16.2 (12.6-19.8)	15.0 (11.8-18.2)	High
4-Forced oxidation, fly ash, soil, adipic	None--100% survival at 100% test concentration	76.6 (56.0-104.8)	Medium(Low)[b]
5-Natural oxidation, fly ash, soil, DBA	69.3 (54.5-84.0)	69.3 (54.5-84.0)	Medium

[a]95% confidence interval in parentheses

[b]EC_{50} within 5% of border line

into the normal tolerance range of Daphnia after 48 hours. Thus, pH was a declining source of stress through the experimental period in these two samples resulting in lower EC_{50}'s than Sample 2 where pH remained high throughout the test period. Using the data for Sample 4, it may be concluded that pH was not the only cause of the observed toxicity in the four samples. In this sample, pH was always well within the tolerance range of Daphnia indicating that the low level of toxicity resulted from other characteristics. Specific conductance measurements indicate levels high enough to cause osmotic imbalance. Since the chemistry for the other three samples is similar to 4, the presence of a relatively high level of TDS can be presumed to contribute to their observed toxicity.

10.3 LEACHING RESULTS

The four samples which were analyzed for biological effects were also leached using the RCRA and ASTM extraction procedures. The RCRA procedure extracts the solids for 24 hours with a solution buffered at pH 5 by acetic acid. The extract is then analyzed for eight metals and six pesticides. The results of these analyses are presented in Table 10-5, along with the RCRA limits. The pesticides analyses was not performed since they would not be expected to be found in an FGD system. As can be seen, none of the analyses exceeds the RCRA limits.

The ASTM extraction procedure contacts the solids for 48 hours with deionized water. No specific analysis are required using this procedure. The analysis performed and the results obtained are presented in Table 10-6. No high values were observed for elements other than the species normally associated with FGD systems (calcium, magnesium, sodium, chloride, and sulfate).

TABLE 10-5. RCRA LEACHATE RESULTS (mg/ℓ)

Element	RCRA Limit	1-Natural oxidation, fly ash, soil	2-Natural oxidation, fly ash, adipic, soil	4-Forced oxidation, fly ash, adipic, soil	5-Natural oxidation, DBA, soil
Arsenic	5.0	0.018	0.004	0.003	<0.003
Barium	100.0	0.65	0.53	1.0	NA
Cadmium	1.0	<0.002	0.02	<0.002	0.045
Chromium	5.0	0.088	0.18	0.02	<0.001
Lead	5.0	<0.002	0.008	<0.002	<0.002
Mercury	0.3	NA	NA	NA	NA
Selenium	1.0	0.038	0.006	0.014	0.005
Silver	5.0	<0.002	<0.01	<0.002	<0.002

NA - not analyzed

TABLE 10-6. ASTM LEACHATE RESULTS (mg/1)

Element	1-Natural oxidation, fly ash, soil	2-Natural oxidation, fly ash, adipic, soil	4-Forced oxidation, fly ash, adipic, soil	5-Natural oxidation, DBA, soil
Aluminum	2.3	1.9	0.12	0.68
Antimony	<0.03	<0.03	<0.03	<0.03
Beryllium	<0.0005	<0.0005	<0.0005	<0.0005
Bismuth	<0.05	<0.05	<0.05	<0.05
Boron	1.5	0.93	0.46	0.62
Calcium	100.	140.	580.	180.
Cobalt	<0.006	<0.006	<0.006	<0.006
Copper	0.008	0.003	0.004	0.005
Gold	<0.03	<0.03	<0.03	<0.03
Indium	<0.05	<0.05	<0.05	<0.008
Iron	0.05	<0.008	<0.01	<0.002
Lithium	0.02	≥	0.05	<0.002
Magnesium	0.20	<0.03	1.7	0.44
Manganese	<0.001	<0.001	0.002	0.019
Molybdenum	0.75	0.75	<0.002	0.38
Nickel	<0.003	<0.003	<0.004	<0.003
Phosphorous	<0.18	<0.18	<0.18	<0.18
Platinum	<0.03	<0.03	<0.03	<0.03
Potassium	78.	91.	0.82	72.
Sodium	22.	21.	0.80	16.
Strontium	0.03	<0.001	0.087	<0.002
Tellurium	<0.1	1.0	<0.1	<0.1
Thallium	<0.1	<1.0	<0.1	<0.1
Tin	0.12	<0.12	<0.12	<0.12
Titanium	0.012	<0.002	<0.005	0.019
Tungsten	<0.03	<0.002	<0.03	<0.03
Uranium	<0.06	<0.060	<0.06	0.06
Yttrium	<0.002	0.002	<0.002	<0.002
Vanatium	0.098	0.017	0.021	0.066
Zinc	<0.003	0.038	<0.003	<0.003
Chloride	12.7	4.7	6.6	29.5
Sulfate	156.	62.5	473.	127.
Conductivity ($\mu mho/cm^2$)	0.75×10^{-3}	1.6×10^{-3}	2.0×10^{-3}	0.95×10^{-3}
pH	10.5	11.1	7.9	10.5

REFERENCES

1. Wang, J.C.S., D.A., Burbank, Adipic Acid Enhanced Lime/Limestone Testing at the EPA Shawnee Test Facility - Second Report, In: Proceedings: Fifth Industry Briefing on IERL-RTP Lime/Limestone Wet Scrubbing Test Programs, EPA-600/7-82-010 (NTIS PB 800199813), August, 1982.

2. Wang, J.C.S., and D.A., Burbank, Adipic Acid Enhanced Lime/Limestone Test Results of the EPA Alkali Scrubbing Test Facility, EPA Technology Transfer Capsule Report, EPA-625/2-82-029, April, 1982.

3. Jarvis, J.B., et al, Effect of Trace Metals and Sulfite Oxidation on Adipic Acid Degradation in FGD Systems, Draft Final Report prepared for U.S. Environmental Protection Agency, IERL-RTP-1386.

4. Burnett, T.A., et al, Economic Evaluation and Comparison of Alternative Limestone Scrubbing Options, In: Proceedings: EPA/EPRI Symposium on Flue Gas Desulfurization, Hollywood, Florida, May, 1980.

5. Anderson, K.D., et al, Definitive SO_2 Control Process Evaluation: Limestone, Lime, and Magnesia FGD Processes, TVA Muscle Shoals, EPA-600/7-80-001, January, 1980.

6. Hatfield, J.D., and Potts, J.M., "Scrubbing with Limestone Slurry: Use of Organic Acids," In: Proceedings: Second International Lime/Limestone Wet Scrubbing Symposium, New Orleans, Louisiana, APTD-1161, June, 1972.

7. Chang, C.S., and G.T. Rochell, "SO_2 Absorption Into $CaO/CaCO_3$ Slurries with Buffer Additives," AICHe 73rd National Meeting, Chicago, Illinois.

8. Federal Register, 1971, Standards of Performance for New Stationary Sources, Vol. 36, No. 247, December 23, pp 24876-24895.

9. Federal Register, 1979, New Stationary Sources Performance Standards; Electric Utility Steam Generating Units, Vol. 44, No. 113, June 11, pp 33580-33624.

10. Federal Register, EPA Continuous Monitor Certificaton Testing, Vol. 44, No. 197, pp 56281

11. Booth, R.L., Handbook for Analytical Quality Control in Water and Wastewater and Wastewater Laboratories, Final Report, EPA-600/4-79-019, PB 297 Cincinnati, Ohio, Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Lab., March, 1979.

12. Environmental Protection Agency, Office of Monitoring Systems and Quality Assurance, Office of Research and Development, Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, QAMS-005/80. Washington, DC, December, 1980.

13. 40 CFR 60 Appendix B "Performance Specification 2," Performance Specification and Specification Test Procedures for Monitors of SO_2 and NO_2 from Stationary Sources, July, 1981.

14. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. 3, Stationary Source Specific Methods, EPA-600/4-77-027b, Research Triangle Park, NC, August, 1977.

15. Jones, G.D., et al, Forced Oxidation Demonstration and Testing at Widows Creek Station Steam Plant (July 1979 through January 1980) Radian Corporation July 18, 1980 Final report to Tennessee Valley Authority, Office of Power.

16. op. cit. Wang, Second Report

17. Ottmers, D.M., Jr., et al, A Theoretical and Experimental Study of The Lime/Limestone Wet Scrubbing Process, EPA 650/2-75-006, EPA Contract No. 68-02-0023, Austin, Texas, Radian Corporation, 1974.

18. Wang, S.C., and Burbank, D.A., "Adipic Acid-Enhanced Lime/Limestone Test Results at the EPA Alkali Scrubbing Test Facility," Presented at the EPA Ind. Briefing, Springfield, Missouri, July 15, 1981.

19. Chang, J.C.S., and Dempsey, J.H., "Pilot Plant Evaluation of By-Product Dibasic Acids as Buffer Additives for Limestone Flue Gas Desulfurization Systems," In: Proceedings: EPA/EPRI Symposium on Flue Gas Desulfurization, Hollywood, Florida, May, 1982.

20. Brusick, D.J., and Yound, R.R., Level 1 Bioassay Sensitivity, EPA-600/7-81-135, Litton Bionetics, Inc., Kensington, MD, August 1981.

21. McCann, J., Choi, E., Yamasaki, E., and Ames, B.N., Detection of Carcinogens as Mutagens in the Salmonella/Microsome Test: Assay of 300 Chemicals, Prc. Nat. Acad. Sci., USA, 72:5135-5139, 1975.

22. Brusick, D.J., et al, IERL-RTP Procedures Manual - Level 1 Environmental Assessment Biological Tests, Draft Report to U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC, 1980.

23. Stephan, C.E., Methods for Calculating an EC , in Aquatic Toxicology and Hazard Evaluation, ASTM STP 634, F.L. Mayer and J.L. Hamelink, (Eds), American Society for Testing and Materials, Philadelphia, PA.

APPENDIX A

LABORATORY PROTOCOL/QUALITY ASSURANCE RESULTS

SECTION 1

INTRODUCTION

The objective of the procedures developed as part of the laboratory protocol for the Adipic Acid Demonstration Program was to generate accurate and reliable data which was responsive to the needs of the program. An additional objective was development of a quality assurance program to assess, document, and ensure the accuracy and reliability of technical work performed as it pertained to both sampling and analysis conducted for this program.

Various aspects of the laboratory protocol developed included:

- sampling techniques,
- analytical methodology,
- data reduction, validation and reporting,
- internal quality control measures,
- laboratory performance audits, and
- preventative maintenance for laboratory equipment and instruments.

A brief description of the various aspects of the laboratory protocol employed will be presented in this appendix. Results of QC data generated during the program will also be presented.

SECTION 2

SAMPLING

Samples were collected daily during the testing period to characterize the scrubber performance and monitor scaling tendencies. This section describes the various procedures used to obtain representative samples.

A sampling and analysis scheduling chart was posted in the laboratory and updated on a regular basis. This provided the laboratory analyst with information as to when various liquid, solid and gas phase samples were to be collected and what analyses were to be performed on the samples. As changes in the objectives of the program were identified, this chart was updated to reflect changes in sampling schedules and analytical requirements.

Listed below are the various sample types collected to characterize the liquid, solid, and gas streams:

- unfiltered liquid sample,
- percent solid sample,
- filtered liquid sample,
- liquid sulfite sample,
- liquid carbonate sample,
- diluted filtrate sample,
- solid phase sample,
- solid phase acid dissolution sample, and
- gas phase impinger solution sample.

A separate sample bottle with affixed label was provided for each sample type collected. Listed on the label was the Radian identification number (obtained from the master log), the sample point code, the sample identifier (date and time), and sample type. Also included on the label were the required weights used to caclulate either sample volume or sample dilution factor. These weights included bottle tare weight, bottle plus reagents weight (both measured prior to sampling) and final bottle weight, measured after sample collection. The calculated dilution factor for diluted filtrate samples was also listed on the label.

Detailed procedures for obtaining liquid phase, solid phase and gas phase samples are described in the "Field Sampling Manual" (DCN 80-213-012-10) prepared for this program. These procedures will be described briefly here.

2.1 LIQUID PHASE SAMPLING

The sampling techniques employed were designed to ensure minimal compositional change during the sampling period. An in-line, positive pressure filtration technique, using a peristalic pump assembly, 142 mm filter holder, and 0.8μ filter was employed on-site to accomplish rapid separation of slurry liquids and solids. Care was taken to ensure that the sampling line and probe had sufficient time to be flushed of previous sample and to equilibrate to the temperature of the sample stream. Sample types which required a filtered sample included diluted filtrate, liquid sulfite, and liquid carbonate.

Further procedures employed to collect liquid phase samples included:

- Sample bottles were thoroughly rinsed prior to sample collection.
- Sampling lines at sample points were purged, where practical, prior to sample collection to ensure a representative sample.

- A portion of sample was used to rinse out the sample bottle and then discarded.
- Sample bottles were filled about 90% full thereby leaving an air space so contents could be easily shaken.

Temperature and pH measurements were made at the sampling location because of the rapid change of these parameters with time. These measurements were made in a flowing sample stream employing a thermometer and calibrated portable pH meter.

2.2 SOLID PHASE SAMPLING

Solid phase samples were also collected daily during the testing period. Weight percent solids determinations of scrubber feed samples were performed to ensure adequate crystal area to meet precipitation requirements and to ensure that solids level did not increase to a point where equipment corrosion would become a problem. Weight percent solids of the thickener feed, underflow, and filter cake were also determined to study the dewatering characteristics of the waste solids.

Solid phase samples were obtained during weight percent solid analyses of slurry samples. After separation, by filtration, from the slurry liquids, the solids were dried in a 50 to 60°C oven. After drying, the solids were stored in a plastic container.

2.3 GAS PHASE SAMPLING

Periodic gas phase sampling was performed, during the testing period, to assess the accuracy of the continuous monitoring equipment. Gas phase species measured included SO_2, C_2, CO_2, CO, and H_2O.

2.3.1 EPA Method 6

EPA Sampling Method 6's were performed once a week at the scrubber outlet to measure SO_2 concentration. Standard EPA Method 6 sampling procedures were followed with the following exceptions:

- Full size impingers were substituted for the midget impingers specified in the EPA procedure. This substitution was made because of the large volume of moisture present in the outlet flue gas.
- An impinger containing isopropanol was not used. This impinger was excluded because of the low SO_3 concentration present in the outlet flue gas had little effect on the measured performance of the FGD system.
- Heat tracing was not used for the sampling tube. Instead, any condensate present in the tube was recovered by purging with air at the completion of the sampling procedure.

Following sampling, total sulfur concentration of the impinger solutions were determined by ion chromatography.

2.3.2 Reich Test

An alternative method used for measuing SO_2 concentrations was the Reich test. This sampling and analysis procedure determines the SO_2 concentration of a metered volume of flue gas by means of the stoichemetric reaction of SO_2 with a known volume of standard iodine solution. A volume of flue gas, measured with a wet test meter is drawn through a gas washing bottle containing standard iodine solution. The SO_2 present in the flue gas stoichimetrically reduces the iodine to iodide. A starch indicator, which forms a blue complex with triiodide, is used to indicate the end point. Figure A-1 shows the Reich test sampling train employed.

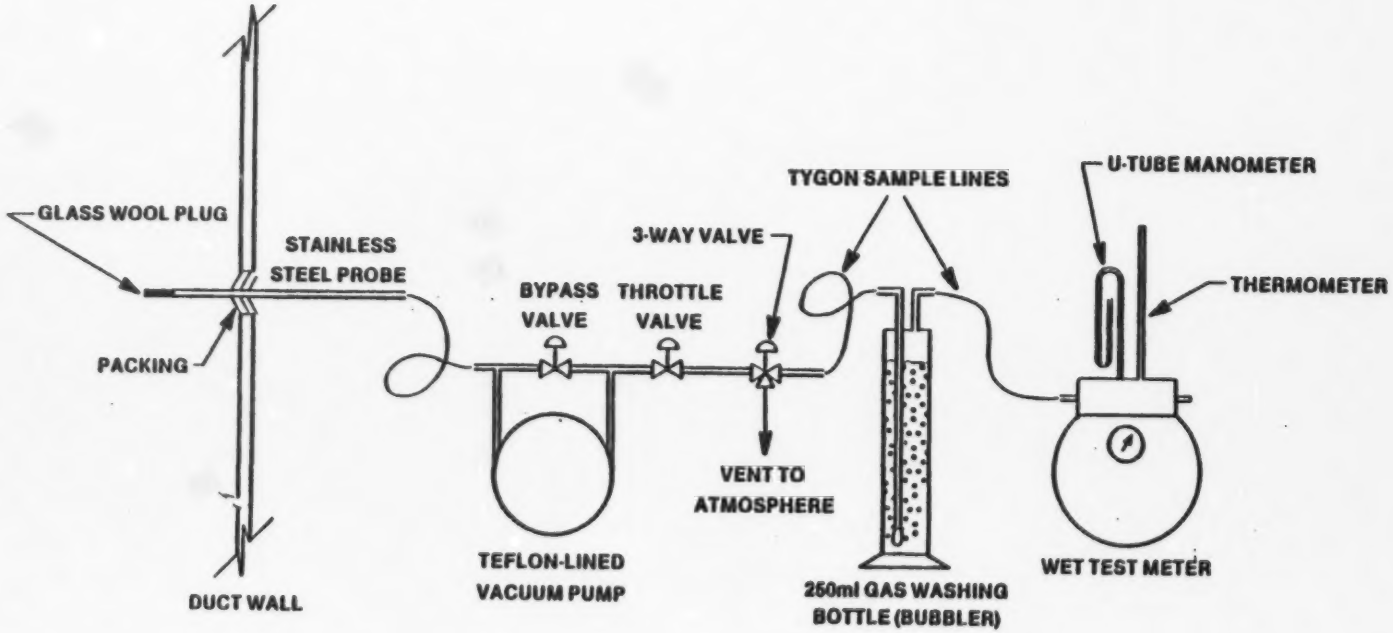


Figure A-1. Reich test sampling train.

2.3.3 Gas Phase Grab Sample

A grab sample of flue gas was extracted from the duct with a two-way hand pump and storeliner "Scotch-Pak" gas sample bag. This sample was subsequently analyzed for O_2, CO_2 and CO concentration employing an Orsat analyzer.

Shown below is the format used for the gas phase Master Sample Log.

Sample ID	Date	Time	Temp. °F	SO_2 PPM	SCFM	Major Components				$\%H_2O$	Particulate gr/SCF	Others
						$\%O_2$	$\%CO_2$	%CO	$\%N_2$			

2.4 PRESERVATION TECHNIQUES

Preservation techniques were employed to ensure that representative samples were analyzed and minimal compositional changes took place between sampling and analysis, and to remove, where possible, species which may interfere with an analysis. The preservation techniques employed are summarized in Table A-1.

2.5 MASTER SAMPLE LOG

A Master Sample Log was maintained to record and document an accurate history of each sample or sample set collected. This was done for the duration of the program. As each sample or sample set was recorded in the log book it was assigned a unique number, normally the next ascending number. Other information included in the log book was the sample point code, the sample identifier (date and time), sample type, the sample tare weight, intermediate weight, final weight, pH and temperature, and any additional comments. A sample page from a typical Master Log is presented in Figure A-2.

TABLE A-1. PRESERVATION TECHNQIUE FOR CHEMICAL MEASUREMENTS

Parameter	Preservation Technique
Liquid Phase	
pH	On-Site Determination
Temperature	On-Site Determination
Sulfite	Filtration, On-Site Determination
Carbonate	Filtration, High pH Buffer Solution
Total Sulfur	Diluted Filtrate, H_2O_2
Chloride	Diluted Filtrate
Nitrate	Diluted Filtrate
Calcium	Diluted Filtrate
Magnesium	Diluted Filtrate
Sodium	Diluted Filtrate
Adipic Acid	Diluted Filtrate
Buffer Capacity	Diluted Filtrate
Solid Phase	
Weight Percent Solids	
Sulfite	Dry Solids
Carbonate	Dry Solids, High pH Buffer Solution
Total Sulfur	Dry Solids, HCl/H_2O_2 Dissolution
Calcium	Dry Solids, HCl Dissolution
Magnesium	Dry Solids, HCl Dissolution
Adipic Acid	Dry Solids, HCl Dissolution

MASTER LOG

Radian #	Sample I.D.	Species	W_1 or pH	W_2 or Temp.	W_3	D.F.	Comments
218	SFD-9/10/80-0845	D.F.	43.10	162.61	237.14	2.30	with H_2O_2
218	SFD-9/10/80-0845	D.F.	45.17	158.42	241.62	2.36	no H_2O_2
218	SFD-9/10/80-0845	LSO_3 (A)	210.11	263.38			25 ml I_2
218	SFD-9/10/80-0845	LSO_3 (B)	216.16	271.92			25 ml I_2
218	SFD-9/10/80-0845	LCO_2	14.38	16.45	45.66		25 ml buffer
218	SFD-9/10/80-0845	pH & Temp.	5.3	48 C			
219	SEF-9/10/80-0900	D.F.	44.17	161.53	239.26	2.51	with H_2O_2
↓	↓	↓	↓	↓	↓	↓	↓

Figure A-2. Master Sample Log

SECTION 3

ANALYTICAL METHODOLOGY

Table A-2 summarizes the analytical techniques employed for the various physical and chemical parameters used to characterize the liquid phase, solid phase, and gas phase samples collected. A more detailed description of the analytical procedures employed for the program is given in EPA Methods for Chemical Analysis of Water and Waste (EPA-600/4-79-020), Standard Methods for the Examination of Water and Wastewater (14th Edition, 1975, APWA-AWWA-WPCF) or in the "Analytical Procedures Manual" (DCN 80-213-012-11) prepared for this program.

A brief summary of the analytical methodology employed for the program is presented below.

3.1 pH

The pH of a slurry sample was determined electrometrically using a glass electrode in combination with a reference potential electrode. Prior to use the pH meter was calibrated with pH 4 and pH 7 buffers and was temperature compensated to the temperature of the slurry sample.

3.2 TEMPERATURE

Temperature measurements were made with a mercury-in-glass thermometer.

3.3 LIQUID PHASE SULIFTE

Sulfite concentration in the aqueous phase, was determined by an iodimetric titrimetric method. During on-site filtration of slurry samples,

TABLE A-2. ANALYTICAL METHODOLOGY

Parameter	Analytical Technique	Reference
Liquid Phase		
pH	Potentrometric, employing glass electrode and potential electrode	EPA 150.1[1]
Temperature	Thermometer	SM 212[2]
Sulfite	Iodometric titration, acetate buffer (pH 6)	APM[3]
Carbonate	Catalytic oxidation, non-dispersive infrared detector, high pH buffer solution	APM
Total Sulfur	Ion chromatography, H_2O_2	APM
Chloride	Ion chromatography	APM
Nitrate	Ion chromatography	APM
Calcium	EDTA Titrimetric	SM 306-C
Calcium	Atomic absorption	EPA 215.1
Magnesium	Atomic absorption	EPA 242.1
Sodium	Atomic absorption	EPA 273.1
Adipic Acid	Ion chromatography	APM
Buffer Capacity	Titrimetric	APM
Solid Phase		
Weight Percent Solids	Gravimetric	APM
Sulfite	Iodimetric titration acetate buffer (pH 6)	APM
Carbonate	Acid digestion, non-dispersive infrared detector	APM
Total Sulfur	HCl/H_2O_2dissolution, ion chromatography	APM
Calcium	HCl dissolution, EDTA titrimetric	SM-306-C
Calcium	HCl dissolution atomic absorption	EPA 215.1
Magnesium	HCl dissolution, atomic absorption	EPA 242.1

(Continued)

[1]EPA Methods for Chemical Analysis of Water and Waste (EPA-60014-79-020)
[2]Standard Methods for the Examination of Water and Wastewater (14th Edition, 1975, PAWA-AWWA-WPCF)
[3]"Analytical Procedures Manual for City Utilities of Springfield Southwest Power Plant" (DCN 80-213-012-11)

TABLE A-2. ANALYTICAL METHODOLOGY (Continued)

Parameter	Analytical Technique	Reference
Solid Phase (continued)		
Adipic Acid	HCl dissolution, ion chromatography	APM
Percent Inerts	Gravimetric	APM
Gas Phase		
Major Components: O_2, CO_2, CO	Orsat Gas Analysis	APM
Flow Rate	S-type pitot, magnehelic gauge	EPA Method 2
Moisture	Condensation, gravimetric	EPA Method 4
Sulfur Dioxide	H_2O_2 impinger solution, ion chromatography	EPA Method 6, APM

a volume of filtered sample was added to a tared sample bottle containing an excess of buffered iodine solution. Upon returning to the laboratory, the sample bottle was reweighed to determine sample volume. Sulfite concentration was then determined by a back titration of remaining iodine following the stoichiometric SO_3 oxidation and iodine reduction. Standard sodium thiosulfate was used as the titrant. Starch was used as an end-point indicator. The SO_3-iodine reaction was buffered at pH 6, with a sodium acetate-acetic acid buffer, to eliminate interference, particularly those encountered in strongly acidic solutions.

ION CHROMATOGRAPHY

Ion chromatography was utilized in the determination of total sulfur, chloride, nitrate, and adipic acid. This method combines the techniques of ion exchange, liquid chromatography, and conductometric detection, for the determination of aqueous ionic species.

A sample is injected into the instrument and is eluted through a system of two ion exchange columns and a conductivity cell. The first column separates the ions in the sample. Each different ion has a characteristic retention time on the column for a given set of conditions. The second column removes the eluent carrier ions thus minimizing the background conductivity of the eluent. Finally, a conductivity cell detector is used to determine the concentration of the ions.

By comparing the sample ions retention times to known standards, specific ions are identified. Standard solutions with known concentration of the ions of interest are run to obtain a calibration curve of peak height (from a strip chart recorder) versus concentration. Sample ion concentrations can then be obtained using the calibration curve.

ATOMIC ABSORPTION SPECTROSCOPY

Atomic absorption spectroscopy was employed to determine calcium, magnesium and sodium concentrations.

This method involves aspirating a liquid sample into an air-acetylene flame where it is vaporized and atomized. Radiation from an appropriate hollow cathode lamp is passed through a monochromator, to a detector, and finally an electronic signal is fed to a digital readout or strip chart recorder where absorption is measured. The absorption for unknown samples is compared to standards of known concentration to obtain sample concentrations. Interferences in the calcium and magnesium determinations were masked by diluting the sample with a lanthanum chloride solution.

ALTERNATE CALCIUM PROCEDURE (EDTA TITRATION)

An alternate EDTA titrimetric method was used to analyze several of the solid and liquid phase samples for calcium. This alternate method was employed to confirm calcium concentrations for samples determined by atomic absorption which were subspect.

Calcium can be determined directly using EDTA when the pH is made sufficiently high so that magnesium is largely precipitated as the hydroxide and an indicator is used that combines only with calcium. The indicator which was employed for this procedure was Murexide (ammonium purpurate). This indicator changes from pink to purple when all of the calcium has been complexed by the EDTA titrant.

ALTERNATIVE ADIPIC ACID DETERMINATION (BUFFER TITRATION)

The adipic acid and DBA concentrations were also measured using a buffer titration method developed by Radian Corporation. The major advantage of this technique is that it does not require ion chromatography equipment which

most utility laboratories do not possess. To obtain the buffer capacity, the pH of a filtered sample is adjusted to 6.0 with NaOH. Then 0.1 molar HCl titrant is added until the sample pH reaches 3.0. By noting the amount of HCl titrant added and running a series of standards in the same concentration range as the sample, the approximate adipic acid concentration can be determined. The buffer capacity measurement will be slightly higher than the actual adipic concentration due to the presence of other species (e.g. carbonate) which also contribute alkalinity and are therefore measured by the buffer method. This method will be most accurate at higher adipic concentrations where the majority of the buffering capacity is due to the adipic acid. However, it can still be used at lower adipic acid concentrations to follow changes in adipic concentrations since the remainder of the buffering species will remain fairly constant compared to adipic. A more complete discussion of this technique is presented in Appendix B of this report.

WEIGHT PERCENT SOLIDS

Weight percent solids were determined by a gravimetric procedure in which an aliquot of sample is filtered through a tared filter paper (Whatman No. 40). The filter and retained solids are dried in an oven set at 50-60°C and reweighed.

SOLID PHASE SULFITE

Sulfite concentrations in the solid phase were determined by an iodimetric titration. A known mass of solid sample is added to a buffered standard iodine solution and allowed to react. The remaining iodine is then back titrated using standard sodium thiosulfate.

ACID DISSOLUTION/PERCENT INERTS

Acid dissolutions were performed on dry solids to analyze for their major soluble constituents. A known mass of solids is added to an acid

solution and allowed to stir for 45 minutes; after which the mixture is filtered through a tared 0.45μ filter. The resulting solution is then analyzed for major constituents. The solids retained on the filter are dried and weighed to determine percent inerts.

ORSAT GAS ANALYZER

Major components of the gas phase, O_2, CO_2, and CO were determined by use of an Orsat gas analyzer.

The Orsat analyzer is pictured in Figure A-3. The analyzer consists of a glass buret for measuring gas volume, a water jacket to maintain constant temperature, a manifold to control gas flow, a leveling bottle to move the gas volume and three abosrption pipettes filled with an abosrbent liquid specific for the gas to be removed.

3.1 CALIBRATION PROCEDURES

Table A-3 presents the calibration requirements employed for atomic absorption spectrophotometric determinations, ion chromatographic determinations, pH measurements, NDIR determinations (carbonate) and gravimetric determinations. Calibration standards were prepared by serial dilution of concentrated certified standards. The analytical balance was calibrated with NBS (Class S) traceable weights.

3.2 DATA NOTEBOOKS

Separate notebooks were used to record data for each analysis type. The format of the data notebooks were designed to organize and present the data in a clear and logical manner. Space was provided to record the complete sample identification, all intermediate values determined during the analysis, and the final analytical result.

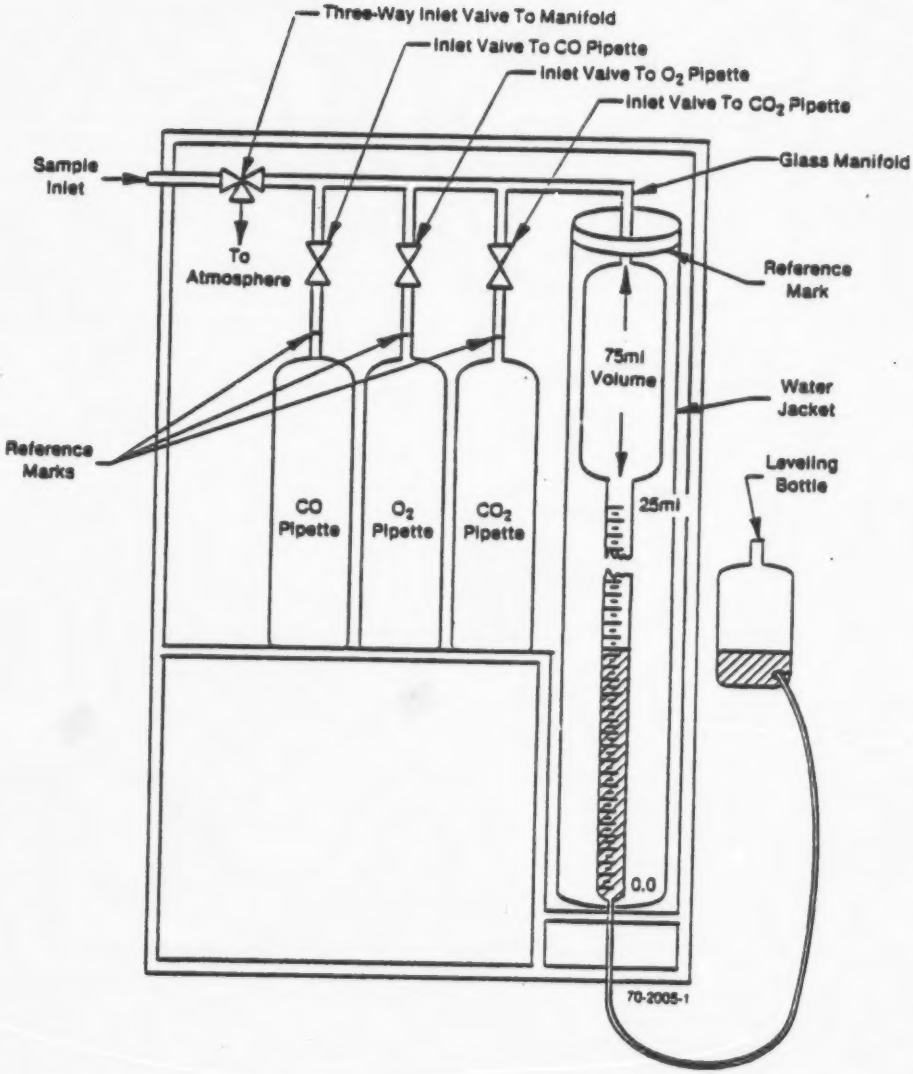


Figure A-3. Diagram of an Orsat analyzer for measuring CO_2, O_2, and CO content of gas samples.

TABLE A-3. CALIBRATION REQUIREMENTS

Analytical Method		Frequency
Atomic Absorption	Multipoint (minimum of three)	1/sample set
Ion Chromatography	Multipoint (minimum of three)	1/sample set
pH	Multipoint (minimum of two)	1/sample set
Non-Dispersive Infrared (Carbonate)	Multipoint (minimum of three)	1/sample set
Gravimetric	Analytical Balance Multipoint (NBS traceable weights)	1/month
Buffer Capacity	Multipoint	1/sample set

Examples of the format used for the various analysis types are presented below:

Ion Chromatography Notebook

Sample ID	Bottle DF	Dionex DF	Peak Ht	Inj. mmole/ℓ	Total mmole/ℓ	Anion or RT	Operator Initials

Bottle DF = dilution factor of sample in bottle

Dionex DF = Dilution required to run on Dionex

Peak Ht = measured peak hieght (mm)

mmole/ℓ, inj. = concentration measured from standard curve

mmole/ℓ, total = mmole/ℓ, inj. × Bottle DF × Dionex DF

Anion = species being measured or Retention Time if species is unknown

Atomic Absorption Notebook

Sample ID	Bottle DF	AA DF	Peak Height	Inj.	Total ppm	mmole/ℓ	mmole/g

Liquid Sulfite

	I	F	N	B	S	B-S	
Sample ID	Bottle Initial Wt.	Bottle Final Wt.	S_2O_3 Normality	Initial Buret Rd.	Final Buret Rd.	Sample mℓ S_2O_3	$\frac{(B-S)(N)500}{F-I}$ mmole/ℓ $SO_3^=$

Solid Sulfite

Sample ID	Tare Wt.	Tare and Sample Wt.	W Sample Wt.	N $S_2O_3^=$ Normality	B Initial Buret Rd.	S Final Buret Rd.	B-S Sample mℓ S_2O_3	$\frac{(B-S)(N)}{2W}$ mmole/g $SO_3^=$

Weight % Solids

Sample ID	B Filter Wt.	A Filter and Solids Wt.	D Bottle Wt.	C Bottle and Sample Wt.	$\frac{(A-B)}{(C-D)} \times 100 =$ Wt. % Solids

Solid Dissolutions and % Inerts

Sample ID	Tare Wt.	Tare and Sample Wt.	C Sample Wt.	Conditions	A Initial Filter Wt.	B Filter and Inerts Wt.	$\frac{(B-A)}{C} \times 100 =$ % Inerts

Data sheets were also developed and employed for the various gas phase sample collection and analyses performed. The format of these sheets provided space to record all necessary data and simplified calculations. After being completed the gas phase data sheets were stored in a 3-ring binder.

SECTION 4

DATA REDUCTION, VALIDATION AND REPORTING

A data flow protocol was developed to ensure that, upon completion of analyses, data was validated and reported in a timely and accurate manner. Figure A-4 is a simplified diagram of the requisite data flow. It was the responsibility of the lead chemist on-site to validate and summarize the analytical data on a daily basis. He performed spot checks on all calculations and scrutinized quality control results to ensure that they were in acceptable variances. Data was summarized in the "analytical results summary" notebook (see below).

				Liquid Phase mmole/ℓ								
Sample ID	pH	Temp.	Wt. % Solid	Ca	Mg	Na	Cl^-	NO_3^-	$SO_4^=$	$SO_3^=$	$CO_3^=$	Adipic (ppm)

	Solid Phase mmole/g						
Sample ID	Ca	Mg	$SO_4^=$	$SO_3^=$	$CO_3^=$	% Inert	Adipic (ppm)

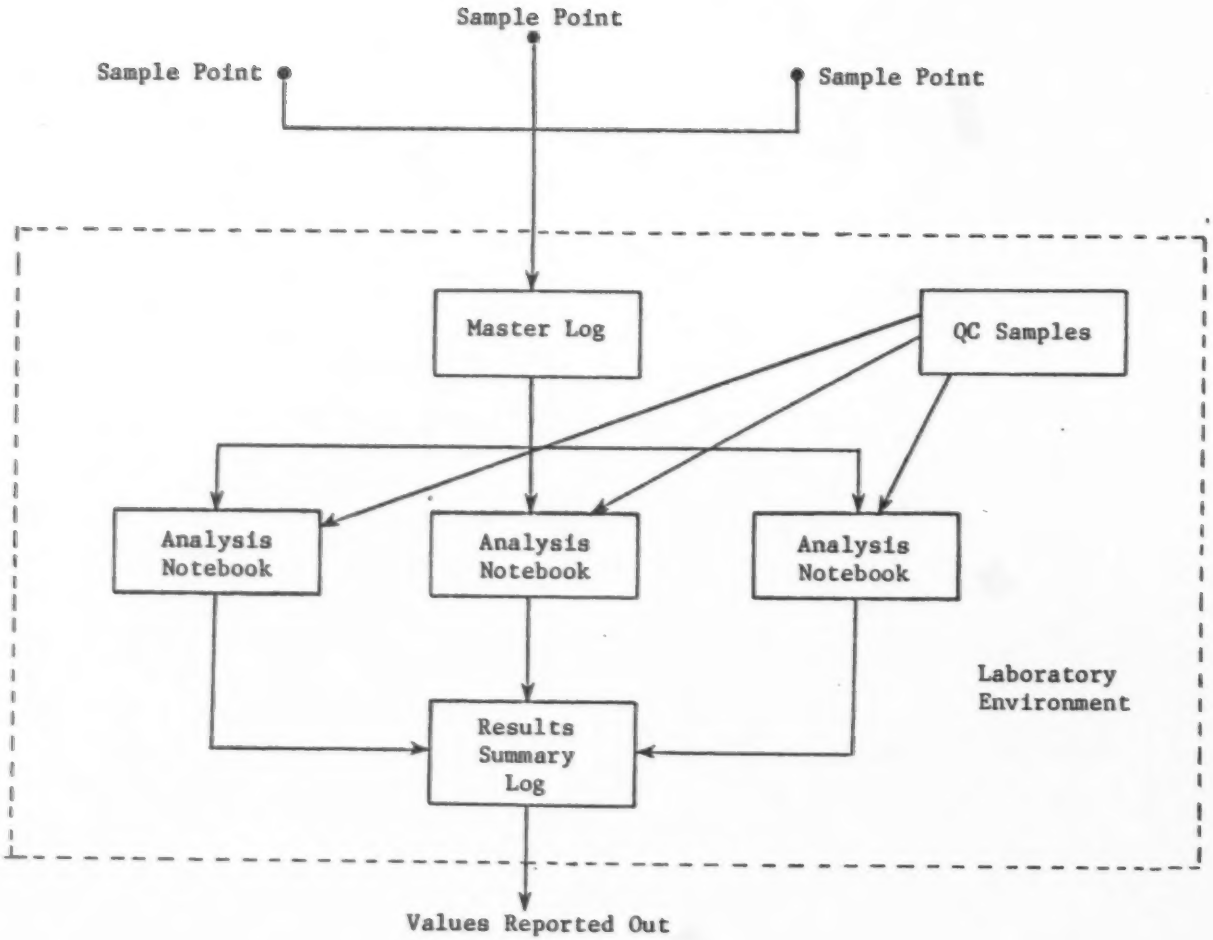


Figure A-4. Data Flow

This was a bound notebook kept in the laboratory. It was divided into two parts, liquid phase results and solid phase results. Data was also transferred onto summary sheets which were given to the engineer on-site for review and ultimately transferred to Austin to be stored on computer data files.

The criteria used to validate data was based upon representative process conditions during sampling, acceptable sample collection and preservation procedures, consistency with other and/or expected results, and adherence to prescribed analytical QC procedures. Solid phase data was evaluated for ion balance between measured cations and anious, expected oxidation percent at steady state (calculated from sulfite and total sulfur concentrations) and expected limestone utilization rates at steady state. Any data found to be suspect, based on these criteria, was identified with respect to the nature of the problem. In most cases the suspect analysis was redone.

SECTION 5

INTERNAL QUALITY CONTROL CHECKS

Quality control procedures were performed and quality control samples were analyzed on a routine basis as part of the analytical protocol for the program. Table A-4 summarizes the type and frequency QC analyses which were performed. The daily QC procedures performed ensured that data generated was both precise and accurate. Upon completion of an analysis, QC procedures were reviewed and generated QC data was plotted by the analyst performing the analysis. This provided the analyst with immediate feedback as to the reliability of the generated data. If data was found to be suspect, based on an unusually large variance of the QC recovery, the analysis was repeated.

Specific details of quality control procedures are given below:

- Calibration Standards

  For analyses which require the production of calbiration curves, the accuracy of data generated can be directly related to properly prepared standards and correct calibration procedures. Calibration standards were analyzed each time an analysis was performed. The calibration curves were plotted along with a mathematical determination of correlation coefficient, slope, and intercept using the method of least squares. The calibration curves and mathematical functions were reviewed to ensure that curves were linear and the normally encountered slope was obtained.

- Blanks

  Blanks were analyzed to provide information on possible contamination of samples by the preparative methodology and to provide background concentration levels of the species in the solutions used in sample preparation.

- Quality Control Standards

  The quality control standards were obtained either from traceable EPA standards for mineral analyses, or were prepared from known concentrations of certified standards. The QC standards had the

TABLE A-4. TYPE AND FREQUENCY OF QUALITY CONTROL ANALYSES

Type of Analysis	Atomic Absorption	Ion Chromatography	NDIR (Carbonate)	Titrimetric (CA^{++},B.C.)	Sulfite	pH	Gravimetric
Calibration Standards (Set)	1/Sample Set	1/Sample Set	1/Sample Set	1/Sample Set	----------	1/Sample Set	1/month
Blank	1/Sample Set	1/Sample Set	1/Sample Set	1/Sample Set	1/Sample Set	----------	----------
QC Standard	1/Sample Set	1/Sample Set	1/Sample Set	1/Sample Set	----------	----------	----------
QC Sample	1/Sample Set	1/Sample Set	1/Sample Set	----------	----------	----------	----------
Duplicate Analysis	1/Sample Set	1/Sample Set	1/Sample Set	1/Sample Set	All Samples	----------	----------
QC Audit Samples	2/Program	2/Program	----------	----------	----------	2/Program	----------

following characteristics: (1) they contain species in the same concentration range as the samples analyzed; (2) the concentrations of the species in the QC sample are accurately known; and (3) the species concentrations do not vary over time.

- Quality Control Sample

  QC samples were generated by obtaining a large volume of sample from a process stream, analyzing this sample initially, and then comparing this result to repeated analyses of the sample over a period of time. The advantage of a QC sample is that it came from an actual process stream and therefore contains all species of interest. Also if changes take place in species concentrations with time it will become evident in analyzing the QC sample.

- Duplicate Analysis

  Duplicate analyses were performed to determine analytical precision. Also for sulfite determinations, in which interferences or error may be a problem, all samples were analyzed in duplicate to ensure accuracy.

- Quality Control Plots

  As QC data was generated in the laboratory it was plotted. This served two functions. First, it provided a visual record of laboratory performance. Second, it facilitated in determining when QC results fall outside of acceptable error limits.

SECTION 6

SUMMARY OF QUALITY CONTROL DATA

6.1 QUALITY CONTROL STANDARDS

Table A-5 presents the results of quality control standards analyzed for calcium, magnesium, sodium, sulfate, and chloride during the course of the program. Figures A-5 through A-9 are the graphical presentations of this data. The approach taken for these quality control charts is to evaluate percent recorvery:

$$P = \frac{\text{observed}}{\text{true}} \times 100$$

and plot the % recoveries in sequence. The average percent recovery ($\overline{P}$) for each parameter as well as standard deviation for percent recovery (Sp) is then calculated. The warning limits for each parameter (95% confidence limit) and control limits for each parameter (99% confidence limit) are determined as:

$$\text{Warning limits} = P \pm 2\ Sp$$

$$\text{Control limits} = P \pm 3\ Sp$$

6.2 QUALITY CONTROL SAMPLES

As previously stated, QC sample data was generated by obtaining a large volume of sample from a process stream and analyzing this sample repeatidly over a period of time. During the course of the program several QC samples were generated and analyzed for calcium, magnesium, sodium sulfate, chloride, nitrate, and adipic acid. This data is presented in tabular form in Table A-6.

TABLE A-5. SUMMARY OF QC STANDARD RESULTS[1]

	QC Standard I.D.					
	QA #1	QA #2	QC #5	STD A	Blind STD #1	Blind STD #2
Calcium						
True Conc.	40.6	5.3	38.3	30	62.5	27.8
Times Analyzed	16	4	5	1	1	1
Observed Conc.						
Mean	40.3	5.3	38.6	30	63.7	29.4
St. Dev.	0.64	0.34	0.49	-	-	-
Magnesium						
True Conc.	8.4	1.8	5.6	-	-	-
Times Analyzed	9	2	2	-	-	-
Observed Conc.						
Mean	8.3	1.8	5.8	-	-	-
St. Dev.	0.13	2	0.01	-	-	-
Sodium						
True Conc.	46.6	8.2	-	-	-	-
Times Analyzed	6	3	-	-	-	-
Observed Conc.						
Mean	46.4	8.0	-	-	-	-
St. Dev.	0.99	0.27	-	-	-	-
Sulfate						
True Conc.	93.6	-	-	-	-	-
Times Analyzed	13	-	-	-	-	-
Observed Conc.						
Mean	90.3	-	-	-	-	-
St. Dev.	1.26	-	-	-	-	-
Chloride						
True Conc.	87.9	18.4	-	-	-	-
Timeas Analyzed	5	1	-	-	-	-
Observed Conc.	86.4					
Mean	2.32	18.4	-	-	-	-
St. Dev.		-	-	-	-	-

[1]all concentrations in mg/ℓ

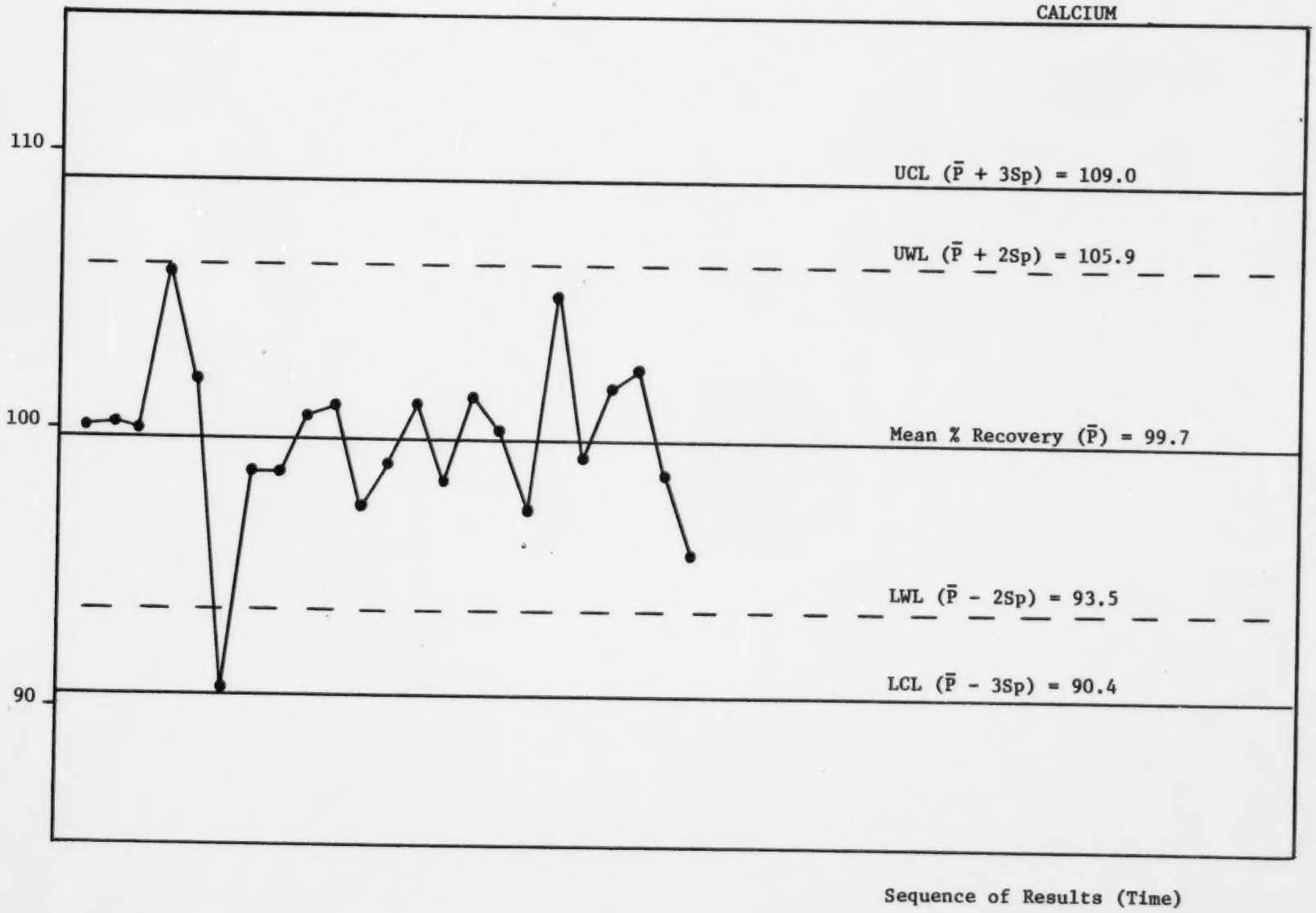


Figure A-5. Quality Control Chart - % Recovery of Calcium Standard

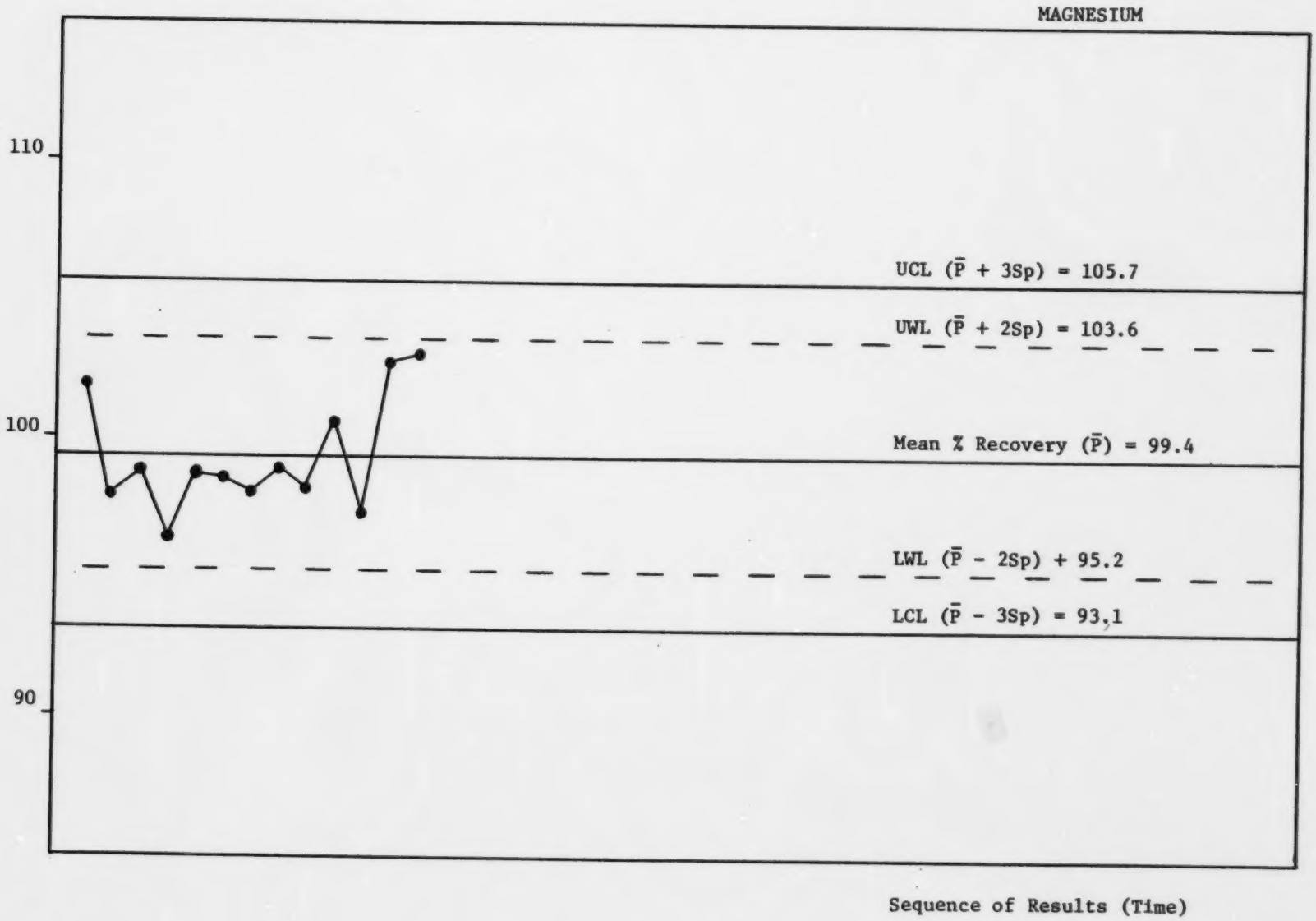


Figure A-6. Quality Control Chart - % Recovery of Magnesium Standard

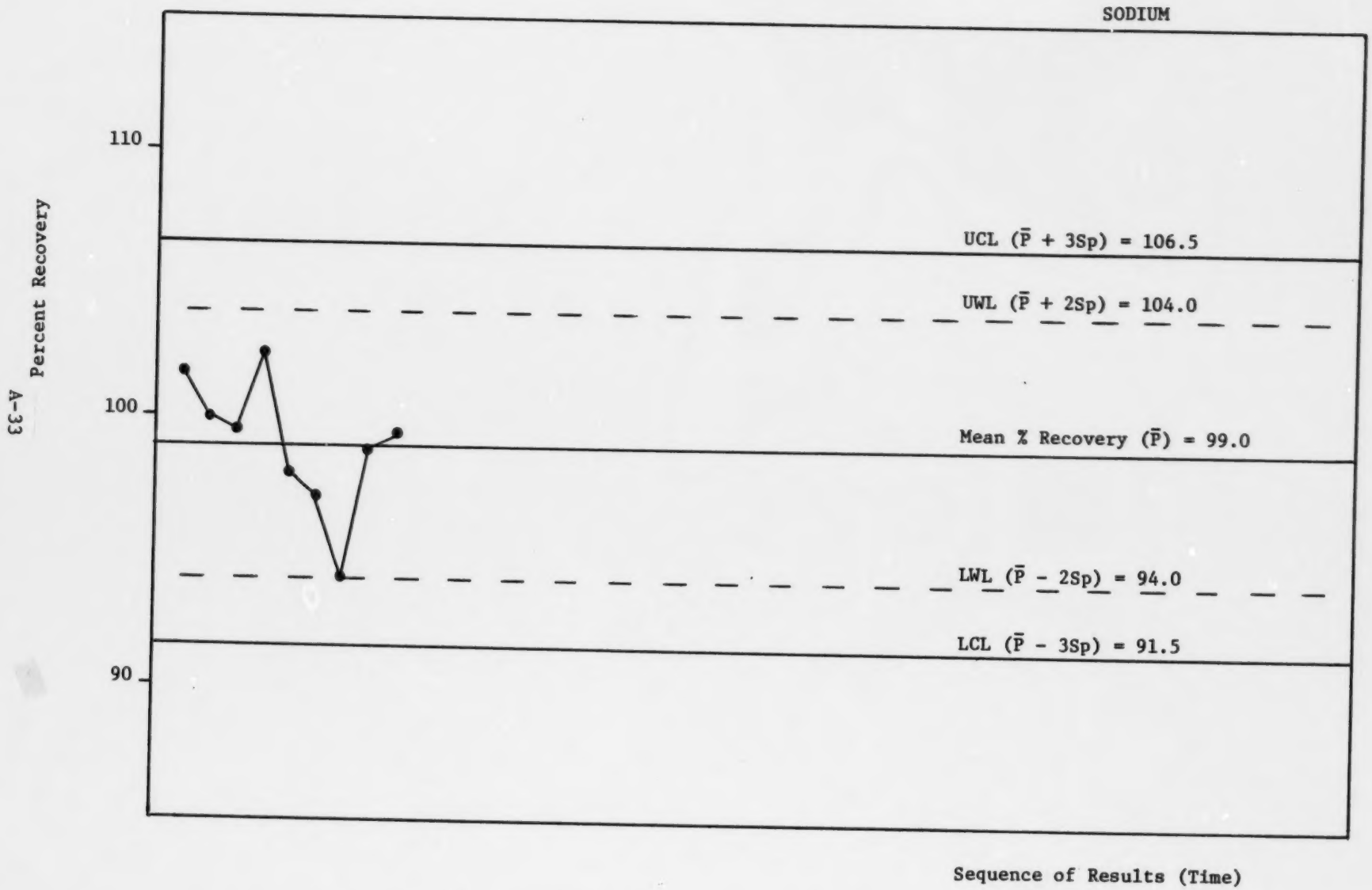


Figure A-7. Quality Control Chart - % Recovery of Sodium Standard

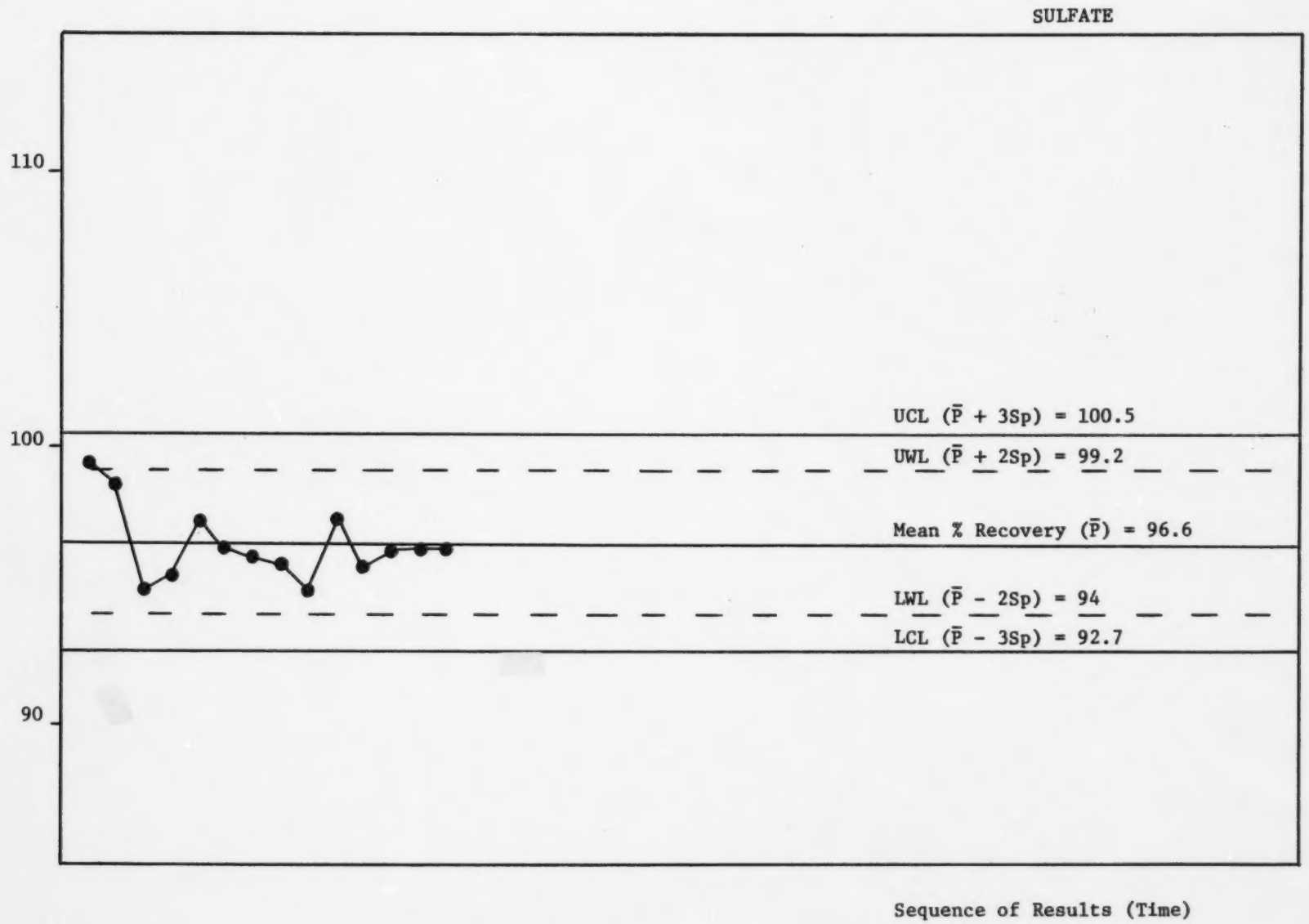


Figure A-8. Quality Control Chart - % Recovery of Sulfate Standard

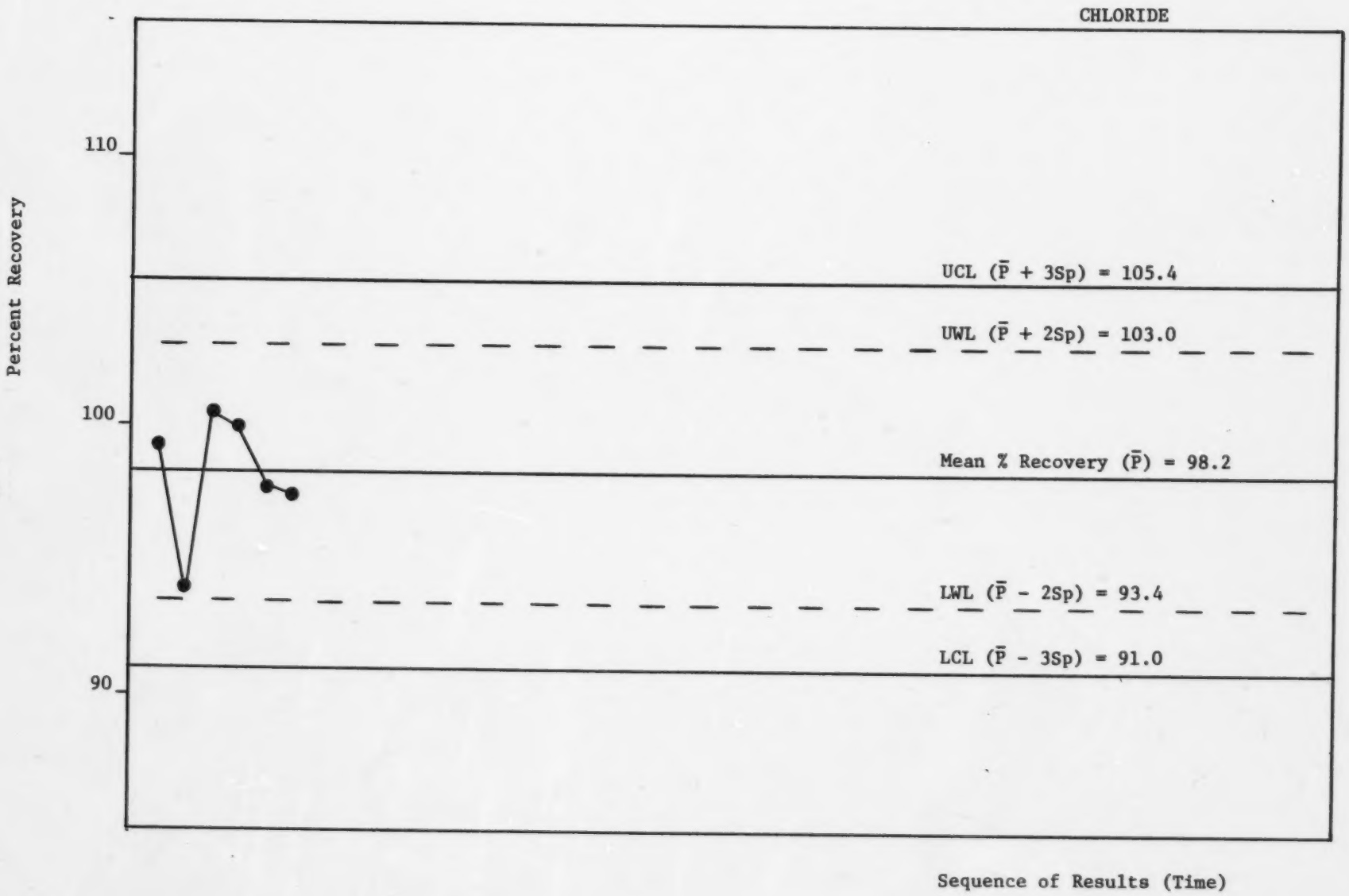


Figure A-9. Quality Control Chart - % Recovery of Chloride Standard

TABLE A-6. SUMMARY OF QC SAMPLE RESULTS[1]

Parameter	Calcium			Magnesium			Sodium		
QC Sample I.D.	Times Analyzed	Mean Concentration	Standard Deviation	Times Analyzed	Mean Concentration	Standard Deviation	Times Analyzed	Mean Concentration	Standard Deviation
QC #1	14	46.1	.94	15	9.73	.30	2	1.07	.00
QC #3	24	45.2	1.01	25	6.13	.13	NA	NA	NA
QC #4	2	17.0	.21	2	3.16	.06	NA	NA	NA
QC #5	30	38.2	1.16	13	5.65	.05	NA	NA	NA

TABLE A-6. (Continued)

Parameter	Sulfate			Chloride			Adipic Acid		
QC Sample I.D.	Times Analyzed	Mean Concentration	Standard Deviation	Times Analyzed	Mean Concentration	Standard Deviation	Times Analyzed	Mean Concentration	Standard Deviation
QC #1	20	15.0	.20	20	78.8	1.28	NA	NA	NA
QC #3	26	12.0	.18	26	62.1	.87	NA	NA	NA
QC #4	5	8.11	.11	5	32.3	.19	NA	NA	NA
QC #5	41	12.8	.25	11	58.9	.93	NA	NA	NA
QC #6	2	13.4	.14	1	57.0	--	46	1141	67
QC #7	16	15.0	.23	NA	NA	NA	27	854	110
AC-J	5	13.1	.38	NA	NA	NA	2	710	85

[1]all concentrations as mg/ℓ

Figures A-10 through A-14 is a graphical presentation of the QC sample data for each parameter. For ease in presentation of all of the data is normalized as percent recovery by dividing the observed concentration, for a particular QC sample by the mean concentration of that sample.

$$\% \text{ Recovery} = \frac{\text{observed conc.}_{\text{QC sample}}}{\text{mean conc.}_{\text{QC sample}}} \times 100$$

The % recoveries are then plotted in sequence. This approach is taken to allow presentation of data, for the various QC samples analyzed for a particular parameter, on a single chart. Also long term trends over the course of the program become evident employing this approach.

The mean percent recovery ($\overline{P}$) and standard deviation of percent recovery (Sp) is given below for each parameter. Since the mean % recovery was calculated by averaging the observed % recovery, this value will be, by definition, 100% in all cases.

Parameter:	Calcium	Magnesium	Sodium	Sulfate	Chloride	Adipic Acid	Nitrate
Times Analyzed	70	55	2	115	62	75	6
Mean % Recovery	100.0	100.0	100.0	100.0	100.0	100.0	100.0
S.D. of % Recovery	2.5	2.2	0.0	1.7	1.4	9.0	5.3

The warning and control limits for each parameter are determined as:

$$\text{Warning limits} = \overline{P} \pm 2\ Sp$$

$$\text{Control limits} = \overline{P} \pm 3\ Sp$$

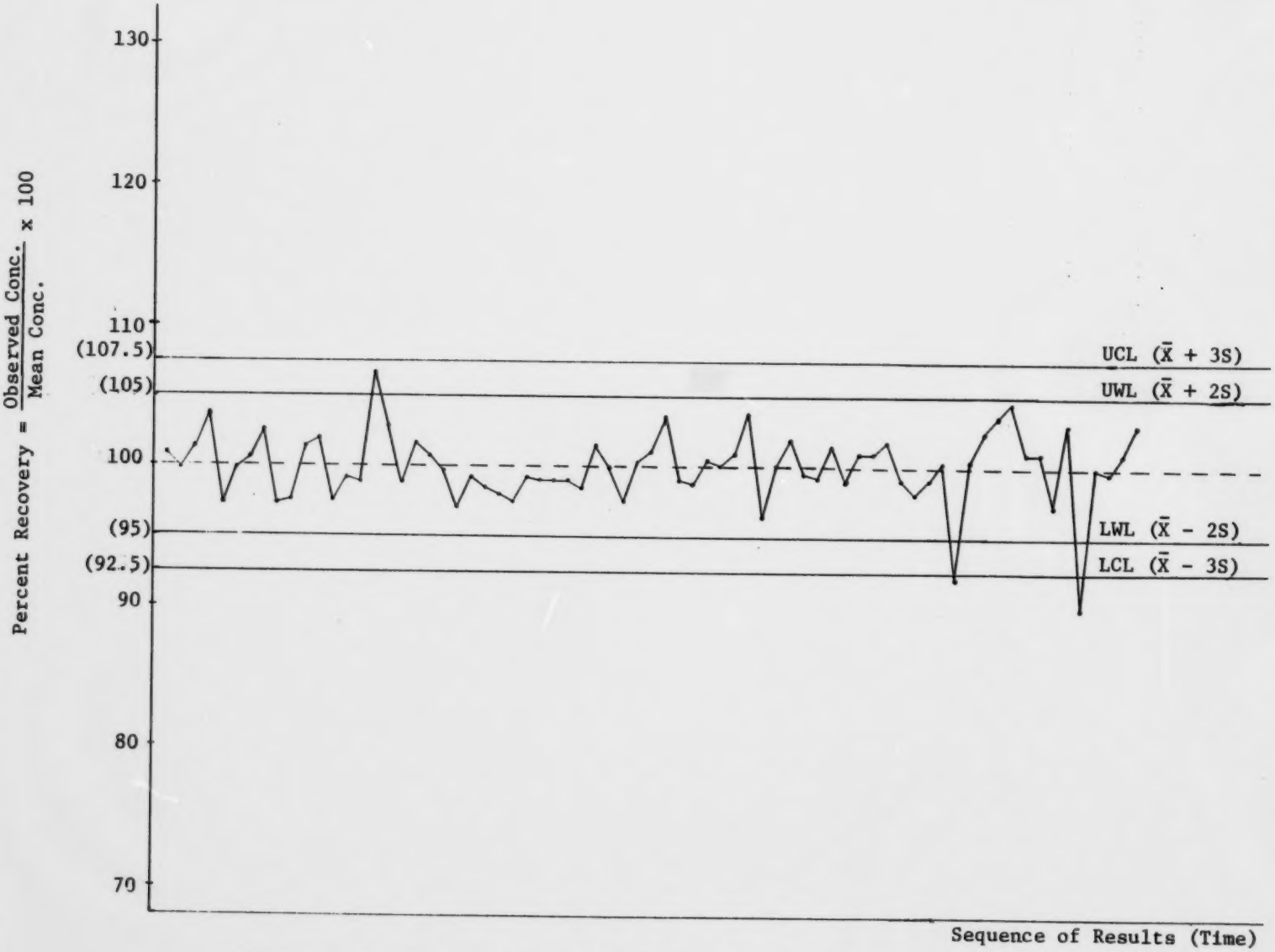


Figure A-10. Quality control chart-replicate sample analysis for calcium.

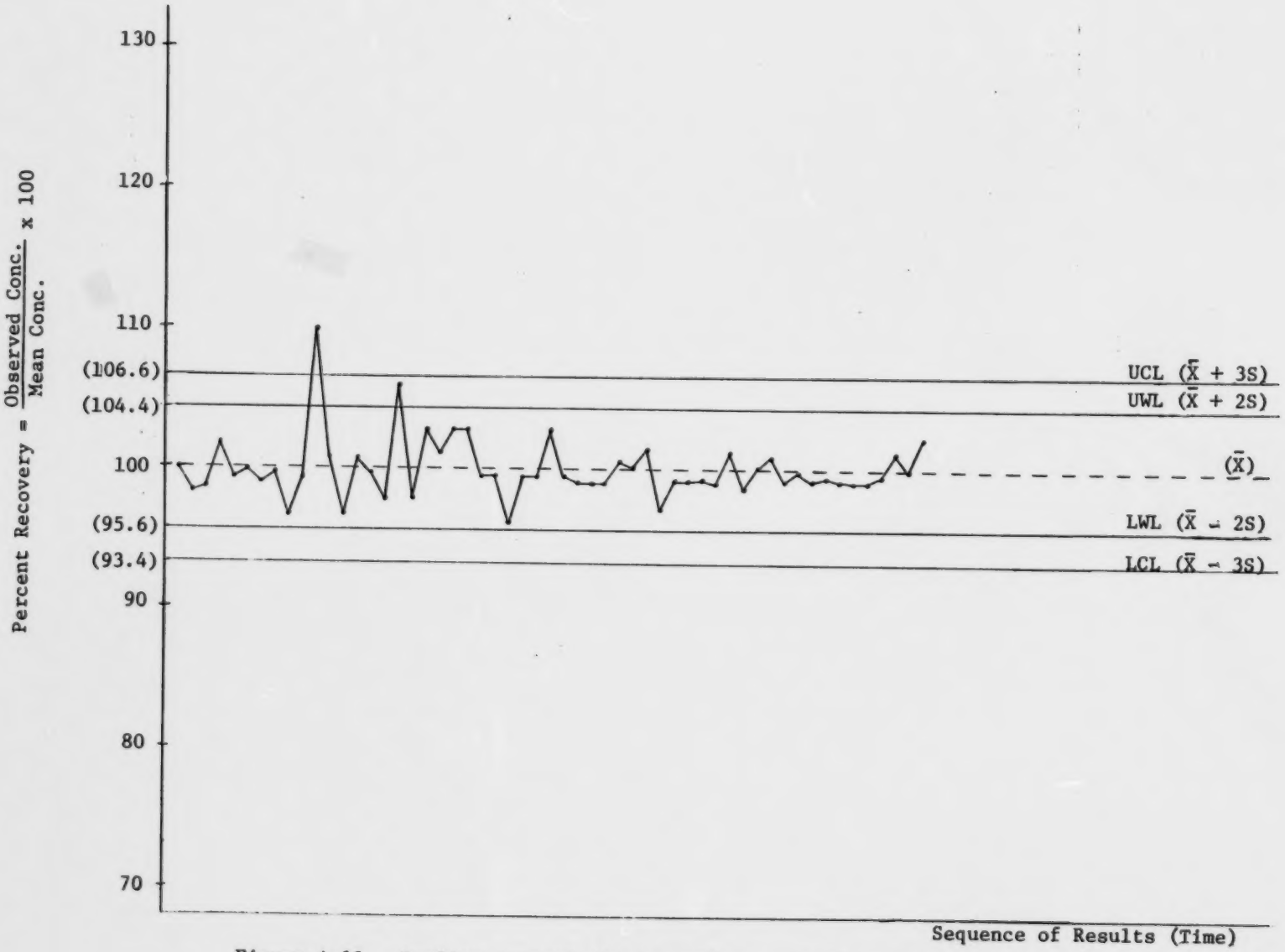


Figure A-11. Quality control chart-replicate sample analysis for magnesium.

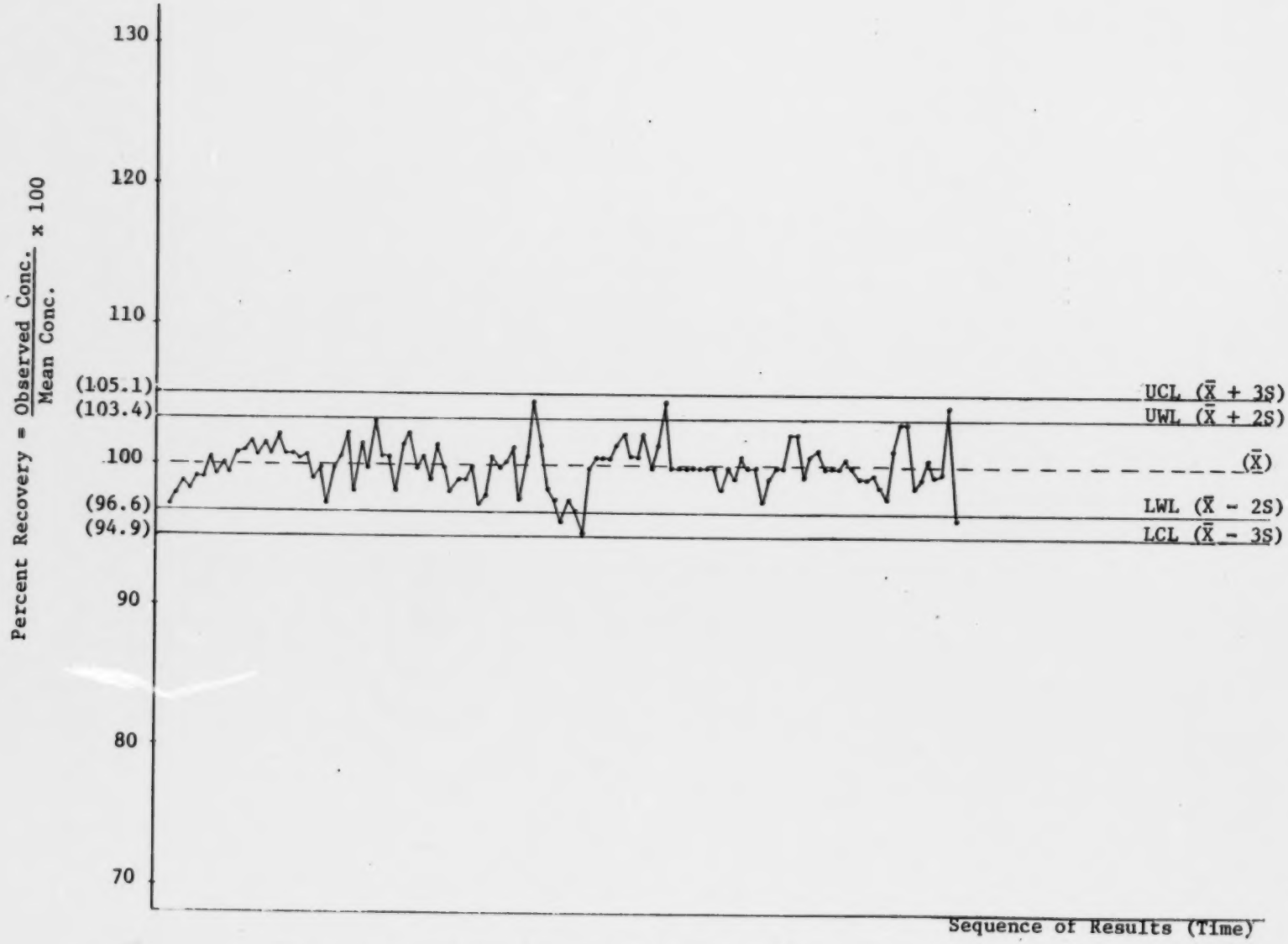


Figure A-12. Quality control chart-replicate sample analysis for sulfate.

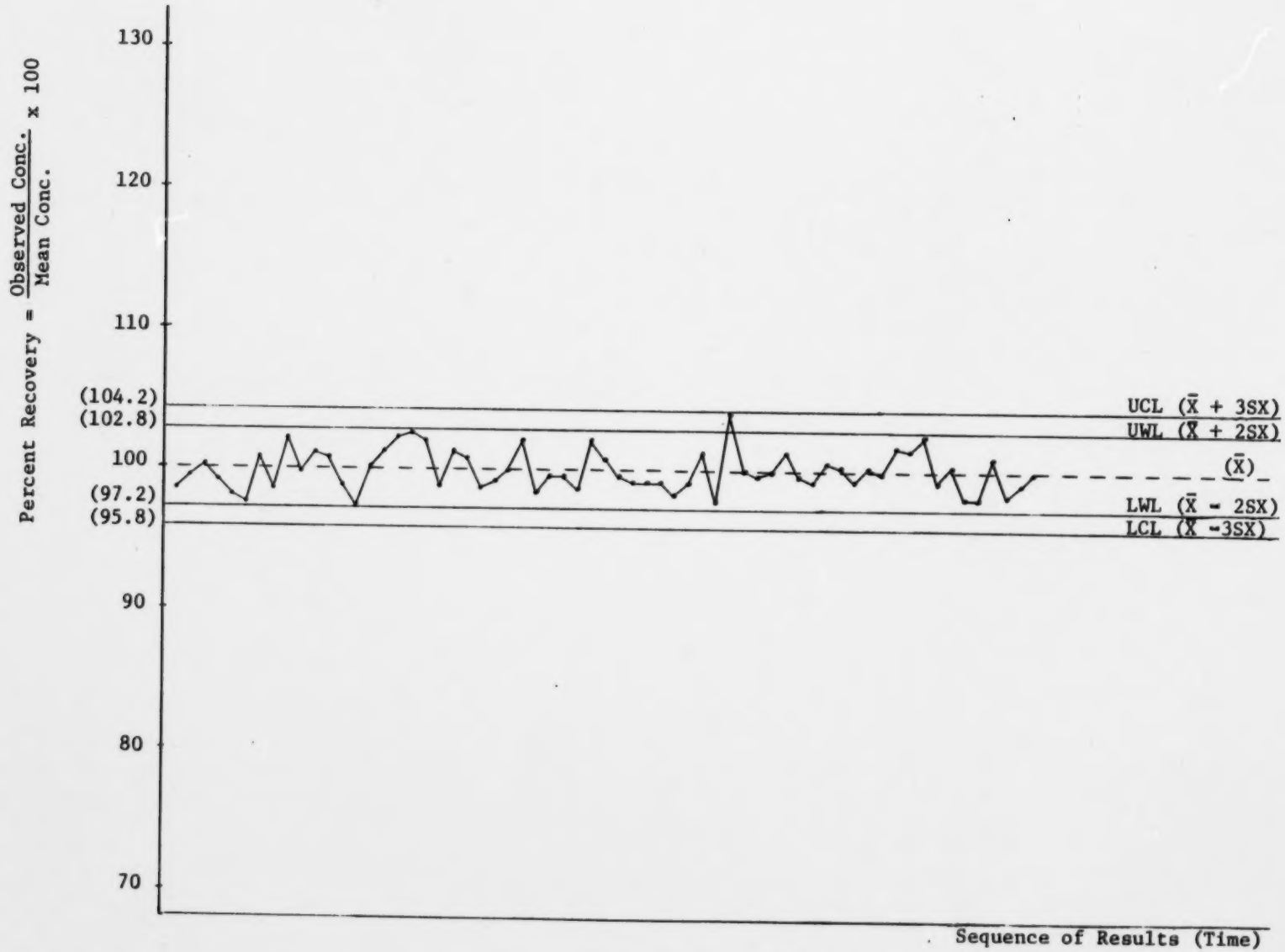


Figure A-13. Quality control chart-replicate sample analysis for chloride.

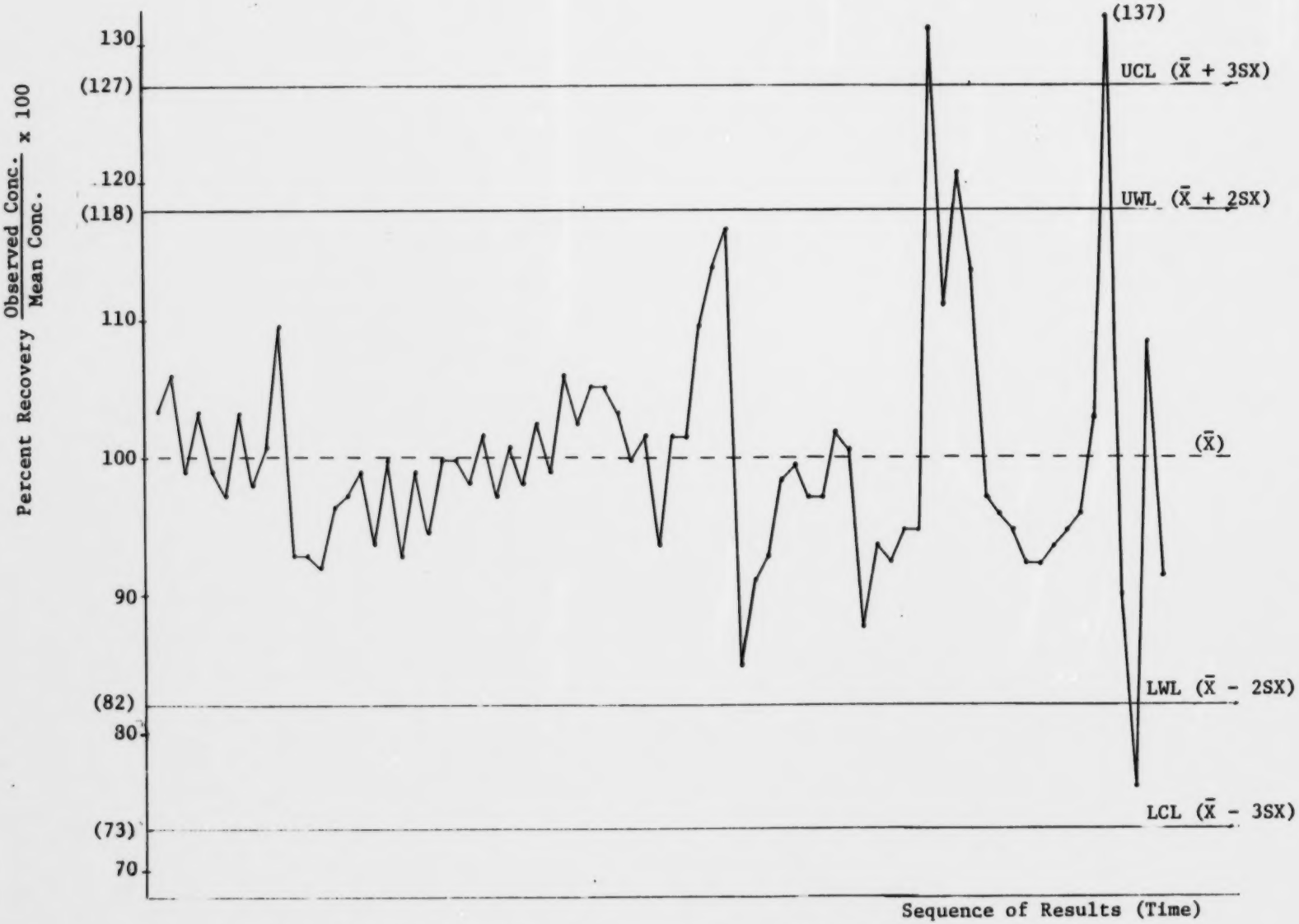


Figure A-14. Quality control chart-replicate sample analysis for adipic acid.

SECTION 7

LABORATORY PERFORMANCE AUDITS

Broadly defined, a laboratory performance audit is an independent assessment of laboratory performance. Two types of laboratory performance audits were employed for this program. The first was analysis of traceable standards prepared outside the laboratory and submitted into the laboratory as blind samples. These standards were prepared in Austin and consisted of EPA Quality Control Standards for Mineral Analysis. They were analyzed on site for calcium magnesium, sodium, chloride, sulfate and pH. Tables A-7 and A-8 presents the results of analyses of the blind audit standards.

The second method used for auditing laboratory performance was reanalysis of a process stream sample by an outside laboratory, in this case, the Austin laboratories. This audit was conducted twice during the program. Tables A-9 and A-10 presents the results of their analysis.

TABLE A-7. RESULTS OF AUDIT SAMPLE ANALYZED ON-SITE

	Parameter	EPA Value	Radian Reported Value	% Recovery
Sample #1	pH units	8.6	8.65	--
	calcium (mg/ℓ)	40.6	40.1	99
	magnesium (mg/ℓ)	8.4	8.21	98
	sodium (mg/ℓ)	46.6	45.6	98
	chloride (mg/ℓ)	87.9	85.8	98
	sulfate (mg/ℓ)	93.6	90.0	96
Sample #2	pH units	7.7	7.87	--
	calcium (mg/ℓ)	5.3	5.46	103
	magnesium (mg/ℓ)	1.8	1.80	100
	sodium (mg/ℓ)	8.2	7.92	97
	chloride (mg/ℓ)	18.4	18.0	98
	sulfate (mg/ℓ)	7.2	9.24	128

Sample submitted - May 1981

TABLE A-8. RESULTS OF AUDIT SAMPLE ANALYZED ON-SITE

	Parameter	EPA Value	Radian Reported Value	% Recovery
Sample QA-5	Calcium	60.9	60.9	100
	Sodium	69.9	67.8	97
	Sulfate	140.0	137.0	98
	Chloride	132.0	133.0	101
Sample QA-6	Calcium	40.6	40.9	101
	Sodium	46.6	46.6	100
	Sulfate	93.6	88.8	95
	Chloride	87.9	88.0	100

Sample submitted - August 1981

TABLE A-9. RESULTS OF PROCESS SAMPLES ANALYZED ON-SITE AND IN AUSTIN LABORATORIES

	Sample Code #	Chloride mM/g Field		Sulfite mM/g Field		Total Sulfur mM/g Field		Calcium mM/g Field		Magensium mM/g Field		DF
Liquid Phase Samples	153	49.4	46	--	--	13.1	12.2	50.0	38.9	5.2	5.2	2.64
	158	62.2	58	--	--	18.8	48.6	43.9	6.0	6.0	5.6	2.59
	231	90.6	86	--	--	18.2	18.5	55.3	51.3	9.17	8.6	2.31
	235	92.8	90	--	--	27.9	26.7	59.6	59.4	9.14	9.2	3.61
	462	NA	76	--	--	31.2	32.3	69.1	68.5	11.4	11.1	3.76
	548	119	110	--	--	31.-	38.8	93.3	90.8	16.2	17.0	2.51
	838	NA	140	--	--	16.8	15.7	99.0	94.3	NA	18.3	2.78
	853	NA	165	--	--	13.1	18.3	127	106.0	NA	22.0	2.53
Solid Phase Samples	186	--	--	.53	.52	4.19	4.25	6.45	6.74	.001	.010	--
	206	--	--	.05	.048	5.28	5.08	5.93	6.36	.004	.004	--
	336	--	--	.69	.30	5.02	4.81	10.2	6.56	.005	.008	--
	337	--	--	.15	.16	4.93	5.17	8.92	6.16	.002	.003	--
	402	--	--	.34	.19	4.88	4.97	6.00	6.46	NA	.007	--
	547	--	--	1.85	1.82	3.91	3.93	7.77	6.61	.007	.007	--
	855	--	--	2.08	1.93	3.5	3.11	8.72	6.86	NA	.009	--
	919	--	--	2.01	.049	5.46	5.24	6.94	5.91	NA	.003	--
	932	--	--	2.86	3.03	3.23	2.69	8.44	6.76	NA	.004	--
	987	--	--	1.6	2.52	4.36	3.44	6.02	5.96	NA	.005	--
	1004	--	--	2.69	3.24	3.07	2.88	NA	6.44	NA	.006	--
								5.6				
	201	--	--	.42	IS	4.43	4.69*	8.17	6.44	.012	.012	--
	302	--	--	.02	.02	5.12	5.35	5.31	6.14	NA	.005	--
	967	--	--	.02	ND	5.20	5.12		5.76	.006	.006	--

DF = Dilution Factor for Liquid Phase Sample
IS = Insufficient Sample
NA = Not Analyzed
ND = None Detected
*$SO_3^=$ not analyzed, total sulfur reported as $SO_4^=$.

TABLE A-10. RESULTS OF PROCESS SAMPLES ANALYZED ON-SITE AND IN AUSTIN LABORATORY

Sample No.	Adipic Acid (mg/ℓ)	
	Austin	On-Site
SCF-N-0304-1645	2,660	2,670
QC #6	1,080	1,220

SECTION 8

PREVENTATIVE MAINTENANCE

To be able to conduct a successful field program it is necessary to ensure that laboratory equipment and instrumentation operate correctly, and when problems occur they must be corrected quickly. In this regard the following considerations were given to preventative maintenance for this program.

- Radian sampling and analytical equipment is routinely serviced after each field program to restore the equipment to original operating specifications. Prior to a field program all instrumentation is set up and checked for proper operation. At this time any worn or inoperative components are identified and replaced.

- In addition to the instrumentation and apparatus required to support on-site measurements and data evaluation, a substantial inventory of spare parts and supplies is available on-site to minimize down time in the event of breakage and/or failure. Spare parts for the analytical instrumentation included valves, injection ports, tubing, tubing connectors and eluent containers for the ion chromatograph; aspirator capillary and burner head for the atomic absorption spectrometer; and two pH meters and elctrodes. Additionally, necessary hand tools and trouble shooting devices such as tubing flaring unit for the IC, feeler guages, soldering iron, and digital volt-ohm-ammeter was available on-site. Also, a large inventory of spare glassware and miscellaneous small items was stocked in the mobile laboratory.

- The lead chemist on-site also maintained a contact in Austin whereby any additional parts, supplies, or replacement instruments needed could be shipped and received in the minimum possible time. When a major piece of equipment of instrumentation failed and on-site repair not be possible, a replacement was obtained from Austin in one to two days.

APPENDIX B

BUFFER TITRATION FOR LIMESTONE SLURRIES CONTAINING CARBOXYLIC ACIDS

SECTION 1

INTRODUCTION

The addition of adipic acid or other buffering acids to conventional limestone flue gas desulfurization systems enhances the removal of sulfur dioxide by buffering the pH of the scrubber slurry. In order to maintain control over this process, it is necessary to have a routine analytical method for monitoring the quality of the scrubber slurry. Previous attempts have focused on measuring the concentration of adipic acid directly in the system. This approach, however, suffers from two major problems:

- The available procedures for determining adipic acid directly are either inaccurate (silicic acid method) or employ costly equipment, such as gas or ion chromatographs.
- Adipic acid can degrade to form other carboxylic acids that also influence the performance of the system.

Since buffering of the scrubber slurry is essential to efficient SO_2 removal, it seemed appropriate to develop an analytical approach involving the measurement of buffer capacity. A correlation can then be developed to relate buffer capacity measurement to adipic acid or other buffering acid concentrations.

The purpose of this study was to develop and test a titrimetric method for measuring the buffer capacity of a scurbber slurry. Ideally, the method would be simple and rapid, require a minimum of equipment, and account for the effects of acids other than adipic acid.

The experimental work was divided into three phases:

1) Method Development
2) Method Characterization
3) Method Testing

The first phase, Method Development, was concerned with establishing the basic experimental procedure for carrying out the buffer titration. Points that were addressed included: required equipment, preparation and storage of reagents, reagent concentrations, electrode calibration, titration pH range, and data reduction. The second phase, Method Characterization, involved assessing the impact of variables such as salt content, adipic acid concentration, and the presence of degradation products. The last phase, Method Testing, provided a practical demonstration of the buffer capacity method by applying the technique to scrubber solutions from bench-scale and pilot plant operations. The two goals of this phase were:

1) To establish that buffer capacity measurements could be made on "real" samples, and

2) To verify that the buffer capacity of a scrubber filtrate is a reliable indicator of the buffering acid concentration.

SECTION 2

THEORY

The pH of a buffer is governed by the ratio between acid and salt. A solution in which the concentrations are ten times those of another solution will have substantially the same pH, provided the acid/salt ratio remains the same. The amount of added acid or base that each of these solutions can tolerate without alteration of the pH will vary appreciably, however. They are quite different in what is called their buffer capacity; that is, in the quantity of acid or base they are capable of consuming. In general, the buffer capacity is defined as the number of millimoles of strong acid or base required to cause a specific decrease in the pH of a fixed volume of solution.

In its simplest form, the buffer titration merely involves measuring the total volume of titrant used to change the pH of the solution from some initial value to some final value. An overall buffer capacity (B_c) is then calculated according to the following relationship:

$$B_c = \frac{C_t \times V_t}{\Delta pH} \tag{2-1}$$

where C_t is the normality of the titrant in mea/ml, V_t is the total volume of titrant added in ml, and ΔpH = (initial pH - final pH).

If pH versus volume of titrant measurements are made at regular intervals during the course of the titration, the buffering ability of a solution can be described in terms of another quantity called the buffer index (β):

$$\beta = \frac{-dC_A}{dpH} \tag{2-2}$$

where dC_A is the change in the concentration of the acid titrant as it is added and dpH is the corresponding change in pH. (The negative sign occurs because the change in pH on the addition of acid is negative.) Plotting β versus pH (see Figure 2-1) yields information regarding the pH range over which buffering occurs, as well as the pH of maximum buffering capacity and the magnitude (β) of this maximum.

For well-defined systems, containing known concentrations of acids, β can be defined theoretically in terms of the appropriate acid dissociation constants and the hydrogen ion concentration. For a monobasic weak acid, it can be shown that,

$$\beta = 2.3 \left\{ \frac{K_w}{[H^+]} + [H^+] + \frac{C_a K_a [H^+]}{(K_a + [H^+])^2} \right\} \tag{2-3}$$

where C_a and K_a are the analytical concentration and acid dissociation constant, respectively, of the weak acid HA. A maximum value of β is obtained at a pH = pK_a and, at this point,

$$\beta \simeq \frac{2.3}{4} C_a \tag{2-4}$$

For a dibasic weak acid, the mathematics are considerably more complex:

$$\beta = 2.3 \left\{ \frac{K_w}{[H^+]} + [H^+] + \frac{2C_a K_2}{[H^+]\left(1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}\right)} - \frac{C_a [H^+]}{\left(1 + \frac{[H^+]}{K_1} + \frac{2K_2}{[H^+]}\right)^2} \left(\frac{K_2}{[H^+]^2} - \frac{1}{K_1}\right)\left(1 + \frac{2K_2}{[H^+]}\right) \right\} \tag{2-5}$$

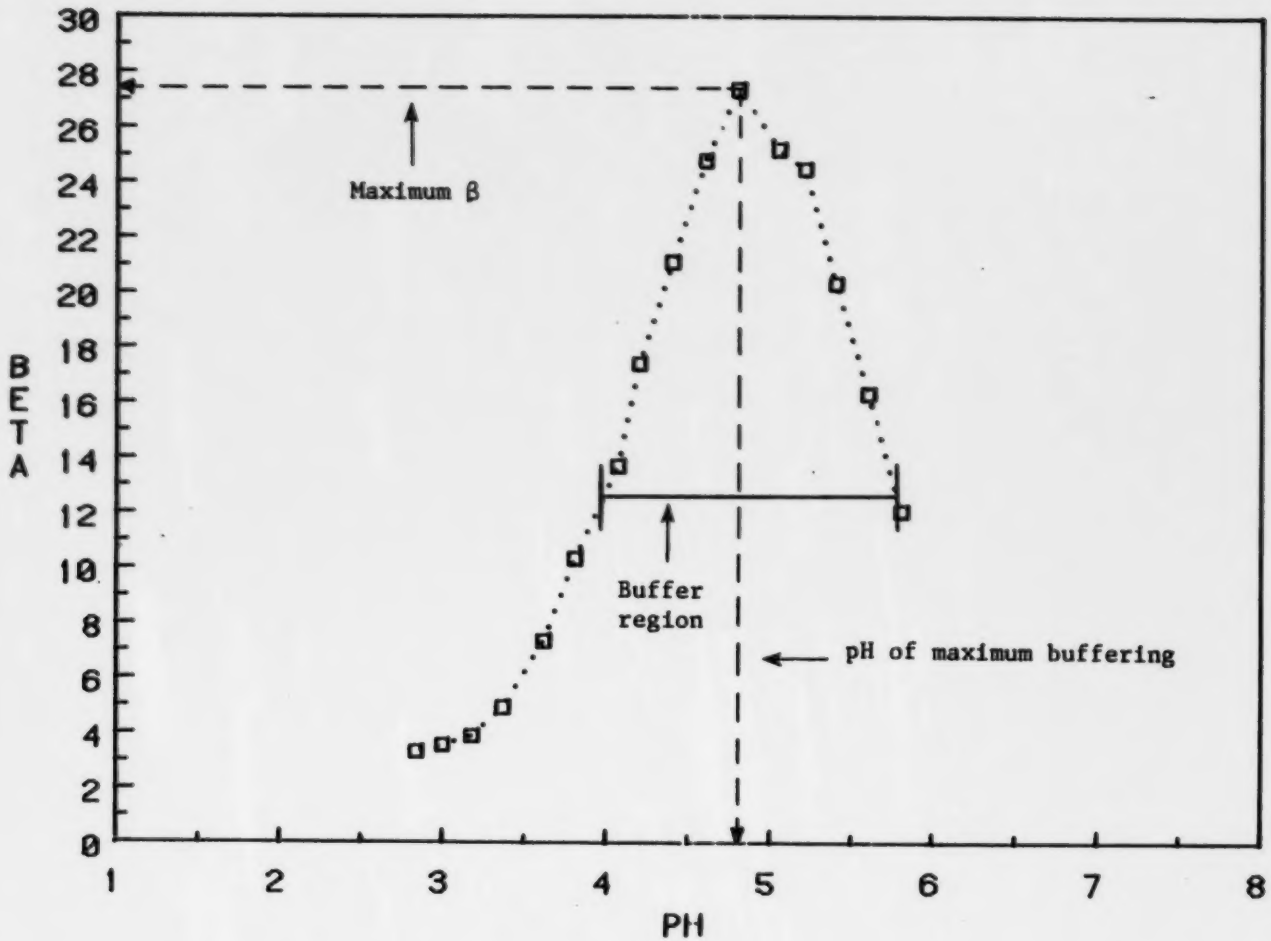


Figure 2-1. Example of Information Provided by a Buffer Index Plot

Because of the two acid dissociation constants involved in equation 2-5, β can exhibit two maximum values at $pH = pK_1 (\beta_{H_2A})$ and $pH = pK_2 (\beta_{HA^-})$. As in the monobasic acid case, each maximum β value is approximated by equation 2-4. If pK_1 and pK_2 are close in magnitude, a single, broad maximum may result due to overlap of β_{H_2A} and β_{HA^-}. This leads to an interesting property of the buffer index. The buffer index of a mixture is the sum of the buffer indexes of each of the acid-base couples present.

e.g.,

$$\beta = \beta_{HA^-} + \beta_{H_2A} \tag{2-6}$$

The property is particularly useful when a solution contains several different acids. In such situations, the buffer index accounts for the combined effects of each acid on the buffering capacity of the solution.

SECTION 3

EXPERIMENTAL

3.1 METHOD DEVELOPMENT

Initially, there were several questions concerning the exact procedure to be followed for the buffer titration including:

- sample size
- titrant concentration
- pH range

Assuming that typical scrubber slurries are about 10 m$\underline{M}$ in adipic acid, it was estimated that reasonable results could be obtained by titrating a 100-ml sample with 0.1 $\underline{N}$ HCl. These estimates were confirmed by subsequent testing.

Selection of the pH range 6-3 for the titration was accomplished by titrating four samples of 10.0 m$\underline{M}$ adipic acid. The initial pH of the sample was adjusted to either 6, 7, 8, or 11 by adding 1 $\underline{N}$ NaOH. Each sample was then titrated down to pH 3, taking pH/volume measurements at intervals of 0.2 pH units. Figure 3-1 shows that the buffer index values are unaffected by the overall pH range of the titration. The results of the four titrations have been overlayed to show that they yield essentially the same size and shape curves.

The pH range of each curve is of course directly related to the pH range of the titration. It is necessary to titrate down to at least pH 3, in order to adequately include the effects of the β's for low pK_a acids such as malonic, oxalic, and formic. The upper end of the pH range was established by calculating overall buffer capacities (equation 2-1) for various intervals covered by the four titrations. Table 3-1 summarizes these results.

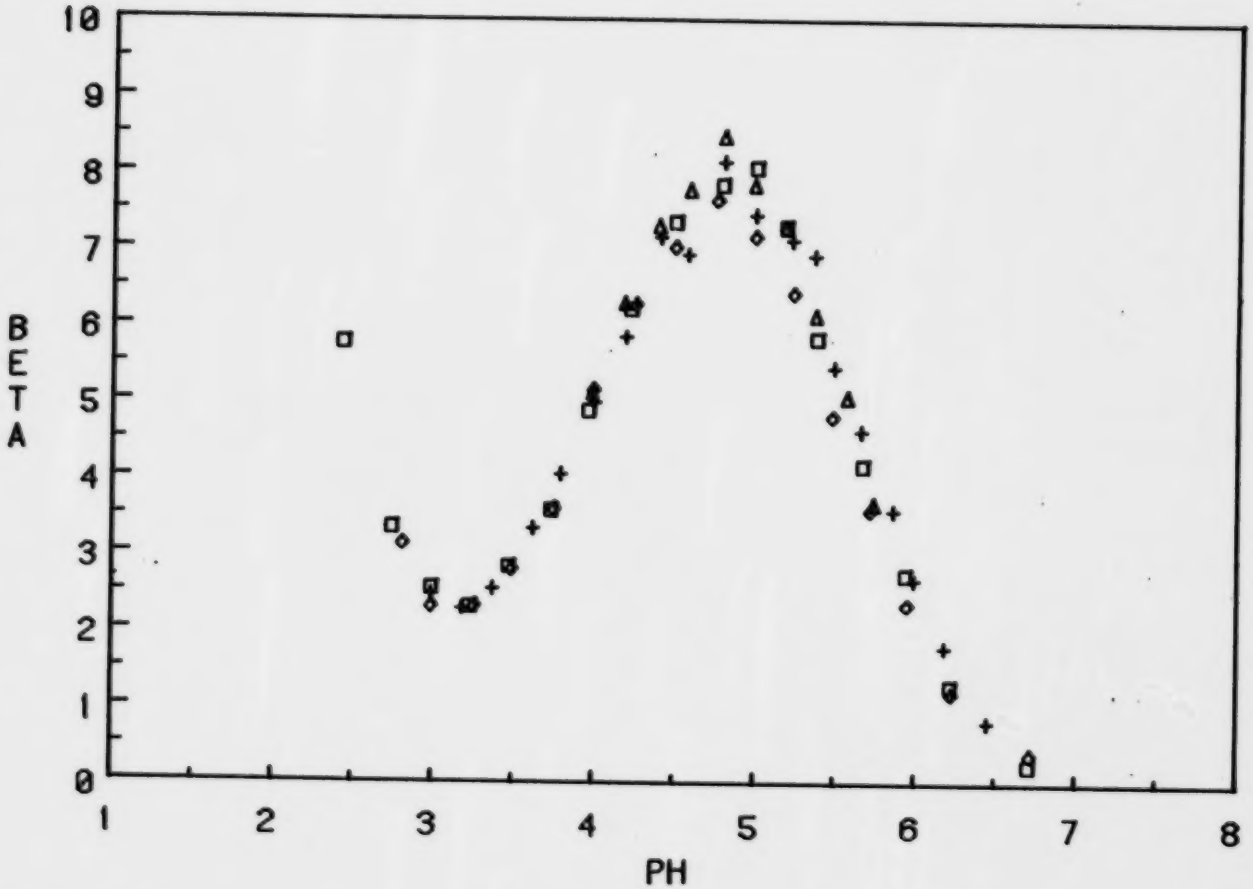


Figure 3-1. Composite plot of buffer index data for 10 m<u>M</u> adipic acid solutions titrated over four pH ranges: Trail #1 (plusses), pH 7-3; Trial #2 (squares), pH 8-3; Trial #3 (diamonds), pH 11-3; and Trial #4 (triangles), pH 6-4.

TABLE 3-1. BUFFER CAPACITY (B_c) VALUES CALCULATED FOR 10 mM ADIPIC SOLUTIONS TITRATED OVER DIFFERENT pH RANGES

	pH Range									
Trial	6-4	6-3	7-4	7-3	8-4	8-3	10-4	10-3	11-4	11-3
#1	7.53	6.40	5.42	5.11	---	---	---	---	---	---
#2	7.66	6.46	6.04	5.52	4.21	4.17	---	---	---	---
#3	7.70	6.49	5.05	4.84	---	---	2.84	3.02	2.55	2.75
#4	7.52	---	---	---	---	---	---	---	---	---
Avg B_c	7.60 ±.09	6.45 ±.05	5.50 ±.50	5.16 ±.34						

Although the range pH 6-4 gave the highest buffer capacity values, the pH 6-3 range gave slightly more reproducible results. Broader ranges of pH are less desirable due to higher uncertainties in B_c.

3.2 TITRATION PROCEDURE

The following method is the titration procedure that was developed and used throughout the remainder of this study:

1) Equipment

- 2 - 25 ml burets
- magnetic stirrer w/stir bar
- pH meter
- glass pH electrode (DO NOT use combination electrode)
- reference electrode (saturated calomel)
- 100 ml pipet
- 250 ml beaker
- ringstand w/buret clamp

2) Reagents

- pH 4 standard buffer solution
- pH 7 standard buffer solution
- 1 N NaOH (prepare using J.T. Baker Dilut-it)
- 0.1 N HCl (prepare using J.T. Baker Dilut-it)

3) Preparation for Analysis

- Calibrate pH meter:

  The pH meter should be calibrated daily using both the pH 4 and pH 7 standard buffers. Between samples, the calibration should be checked with the pH 7 buffer. If the calibration changes more than ±0.02 pH units (i.e., it drifts outside the range of 6.98 - 7.02), the entire calibration procedure should be repeated.

  (a) Set the TEMPERATURE control on the pH meter to room temperature (25°C).

  (b) With the pH meter in STANDBY, rinse the electrodes with DI water and blot dry (DO NOT wipe them, as this can scratch the glass).

  (c) Immerse the electrodes in the pH 7 standard buffer solution, turn on the magnetic stirrer, switch the pH meter to OPERATE, and wait for a stable pH reading of 7.00 (allow 1-2 minutes for the reading to stabilize).

  (d) If necessary, adjust the CALIBRATE knob on the pH meter to obtain a stable reading of 7.00.

  (e) Turn off the magnetic stirrer, switch the pH meter to STANDBY, remove the electrodes from the pH 7 buffer, rinse the electrodes with DI water and blot dry.

  (f) Immerse the electrodes in the pH 4 standard, turn on the magnetic stirrer, switch the pH meter to OPERATE, and wait for a stable pH reading of 4.01 (allow 1-2 minutes for the reading to stabilize).

(g) If necessary, adjust the SLOPE knob on the pH meter to obtain a stable reading of 4.01.

(h) Repeat steps b-g until the two buffer solutions give readings of 4.01 and 7.00 without further adjustment of either the SLOPE or CALIBRATE settings.

- Fill burets:

  (a) Put 1 N NaOH in one buret.

  (b) Put 0.1 N HCl in the other buret.

- Prepare sample:

  (a) Put a magnetic stir bar in a clean and dry 250-ml beaker.

  (b) Pipet a 100 ml aliquot of diluted scrubber filtrate into the beaker (the filtrate should be at room temperature).

  (c) Place the beaker on the magnetic stirrer, turn on the stirrer, and immerse the electrodes in the sample solution.

  (d) Switch the pH meter to OPERATE, wait 1-2 minutes for a stable reading, and record the pH of the sample solution.

4) Analysis

The pH of the filtrate sample is first adjusted to 6 by adding 1 N NaOH. The sample is then titrated to pH 3 with 0.1 N HCl.

- Adjust sample pH to 6:

  (a) Measure the initial level of the NaOH buret to ±0.01 ml and record as $V_{I,NaOH}$.

  (b) SLOWLY add 1 N NaOH dropwise until the pH of the sample solution is ≈6. (Because the NaOH is relatively concentrated, it will be difficult to get a pH of exactly 6.0.

If this is the case, it is preferable to overshoot pH 6 slightly and titrate back to pH 6 with HCl according to step (d).

(c) Rinse the tip of the buret into the sample with a small amount of DI water, record the final buret level as $V_{F,NaOH}$, and record the pH of the sample solution.

(d) If pH 6 was exceeded during the addition of NaOH, switch to HCl buret and SLOWLY add 0.1 N HCl dropwise until the pH of the sample solution is 6.00 ±0.02. Rinse the tip of the buret with a small amount of DI water. Record the pH as pH_I.

- Titrate sample to pH 3:

(a) Measure the level of the HCl buret to ±0.01 ml and record as $V_{I,HCl}$.

(b) SLOWLY add 0.1 N HCl until the pH of the sample solution reaches pH 3.00 (for best results, it is desirable to obtain a final pH of 3.00 ±0.02).

NOTE: If a β vs pH plot will be generated from the data, pH/volume of titrant measurements must be made at ≈0.2 pH unit intervals.

(c) Rinse the tip of the buret with a small amount of DI water. Measure the final level of the HCl buret to ±0.01 ml and record as $V_{F,HCl}$.

(d) Record the pH of the sample solution as pH_F.

SECTION 4

DATA REDUCTION

4.1 BUFFER CAPACITY CALCULATIONS

The buffer capacity (B_c) of a solution is calculated by employing equation 2-1.

$$B_c = \frac{C_t \times V_t}{\Delta pH}$$

where $V_t = (V_{F,HCl} - V_{I,HCl})$ and $\Delta pH = (pH_I - pH_F)$. It must be understood, however, that B_c values may only be compared from one solution to another if the same volume of sample is titrated over the same pH range.

A typical calculation for a 100-ml sample of 10 m<u>M</u> adipic acid would be as follows:

$$B_c = \frac{(0.1 \text{ mea/ml})(21.37 \text{ ml} - 0.55 \text{ ml})}{(6.01 - 3.00)} = 0.692$$

4.2 BUFFER INDEX CALCULATIONS

A buffer index (β) calculation requires slightly more data handling. Before β can be calculated, the instantaneous concentration of titrant in the sample solution (C_{TS}) must be derived from the experimental data regarding the volume of titrant added:

$$C_{TS} = \frac{C_t \times V_t}{V_s + V_t} \qquad (4\text{-}1)$$

where C_t is the concentration of the titrant in mea/l, V_t is the volume of titrant added, and V_s is the initial volume of the sample solution. For

example, if 11.96 ml of 100 m$\underline{M}$ HCl is added to 100 ml of solution then,

$$C_{TS} = \frac{(100\ m\underline{M}) \times (11.96\ ml)}{100\ ml + 11.96\ ml} = 10.68\ m\underline{M}$$

Once C_{TS} values have been calculated for each point of the titration, β can be derived very simply:

$$\beta = \frac{(C_{TS_2} - C_{TS_1})}{pH_1 - pH_2} \qquad (4\text{-}2)$$

where data points 1 and 2 are successive pH/titrant concentration pairs. To illustrate how equation 4-2 would be used:

1) Assume that the pH after adding 11.96 ml of HCl is 4.42, and call this data point 1.

2) Then, $pH_1 = 4.42$

   $C_{TS_1} = 10.68\ m\underline{M}$

3) Assume that the pH after adding 13.88 ml of HCl is 4.21, and call this data point 2.

4) Then, $pH_2 = 4.21$

   $$C_{TS_2} = \frac{100\ m\underline{M} \times 13.88\ ml}{100\ ml + 13.88\ ml} = 12.19\ m\underline{M}$$

5) Substituting into equation 4-2 yields: $\beta = \frac{12.19 - 10.68}{4.42 - 4.21} = 7.19$

4.3 ADIPIC ACID CONCENTRATION CALCULATION

A close approximation of scrubber sample adipic acid concentration can be arrived at by establishing a linear relationship between the buffer capacity of adipic acid standards and scrubber samples. The acid concentration obtained in this way may differ from true acid concentration because of other species present which contribute to the buffering capacity of the sample; i.e., carbonate and sulfite. However, the contribution to buffer capacity of these other species is generally small compared to adipic acid due to the pH range (pH 6 to pH 3) over which the buffer capacity titrations are made. Also, since the concentration of other buffering species in scrubber samples is fairly constant; buffer capacity measurements, while not determining acid concentration on an absolute basis, can provide a means for monitoring acid concentration on a relative basis to control acid addition rates. Finally, since buffer capacity titrations are not specific to any one acid but, instead, will measure the buffering capacity of any acid with a pKa in the pH range 6 to 3, the method can be used to monitor and control acid addition for a wide variety of buffering acids, such as DBA.

For the Adipic Acid Demonstration Program at Springfield MO, a linear relationship between adipic acid concentration and buffer capacity was established by measuring buffer capacity for series of eight adipic acid standard solutions in a concentration range of 200 mg/ℓ to 3000 mg/ℓ. A leasts-square best fit mathematical model established a calibration curve with a correlation coefficient = .9999, a slope = 240, and an intercept = (-70). Thus the relationship for converting buffer capacity (BC) to adipic acid concentration was:

$$\text{Adipic Acid (mg/}\ell) = 240\ BC - 70$$

SECTION 5

EXPERIMENTAL RESULTS

5.1 METHOD CHARACTERIZATION

There are some potential problems that may be encountered in determining the buffer capacity of complex scrubber solutions. This phase of the study was concerned with assessing the impact of three important factors: salt content, the concentration of adipic acid, and the presence of degradation products.

5.1.1 Effects of Salt Content and Adipic Acid Concentration

The effects of salt content and adipic acid concentration were investigated by titrating a series of solutions containing varying amounts of adipic acid and inorganic salts. The relative proportions of Cl^-, $SO_4^=$, Ca^{+2}, Mg^{+2}, and Na^+ were adjusted to produce a range of ionic strengths, a range of calcium concentrations, and a range of magnesium concentrations. In addition, the concentration of adipic acid was varied from 5 m$\underline{M}$ to 50 m$\underline{M}$. Table 5-1 provides a detailed description of the eight test solutions that were prepared and the buffer capacities that were determined.

Performing a linear regression on the B_c versus adipic acid concentration data in Table 5-1 yields a straight line with a slope = 0.616, y-intercept = 0.738, and a correlation coefficient of 0.9997. Thus,

$$[\text{Adipic}] = \frac{B_c - 0.738}{0.616} \qquad (5\text{-}1)$$

The excellent linear correlation for these data is strong evidence that the buffer capacities are not affected by either ionic strength or inorganic salt concentrations.

TABLE 5-1. SUMMARY OF IONIC STRENGTH TEST SOLUTION CONCENTRATIONS AND BUFFER CAPACITY RESULTS

Soln #	Species Concentrations (mM)						Ionic Strength (M)	Buffer Capacity (B_c)
	Adipic	Mg^{+2}	Ca^{+2}	$SO_4^{=}$	Na^{+}	Cl^{-}		
1	4.943	4.971	30.045	15.020	60.073	100.065	0.180	3.52
2	50.014	4.971	30.045	15.020	60.073	100.065	0.180	31.54
3	10.018	20.018	---	59.976	239.935	160.019	0.360	6.92
4	9.984	50.005	---	150.008	600.037	400.031	0.900	7.21
5	9.977	99.989	---	299.978	1199.958	799.980	1.800	7.40
6	10.018	70.008	---	29.985	119.948	199.994	0.360	6.68
7	10.010	49.981	19.996	30.032	120.057	199.987	0.360	6.71
8	9.995	60.013	9.984	30.020	119.990	199.944	0.360	6.78

Plots of β vs pH for each titration yield additional information concerning the effects of these variables on the behavior of β. Figure 5-1 compares the results with solutions #1 and #2, which only differed in adipic acid concentration. Other than the expected effect of adipic acid concentration on the magnitude of the β values, the two curves are similar in shape and location. Figure 5-2 combines the results obtained with solutions #3, #4, and #5. Here there is a pronounced effect due to variations in ionic strength. As the ionic strength increases, the effective pK's of adipic acid decrease and this is translated into a corresponding decrease in the pH maximum of the β vs pH curve. At an ionic strength of 0.360 (solution #3), the β_{max} occurs at about pH 4.65. Whereas at an ionic strength of 1.800 (solution #5), the β_{max} occurs at about pH 4.40. Figure 5-3 shows the results of titrations on three solutions differing only in their relative concentrations of calcium and magnesium. It is very apparent that neither of these variables has any effect on the β curves.

5.1.2 Effects of Degradation Products

A survey of the behavior of eight different carboxylic acids was conducted by titrating individual solutions of each acid. Table 5-2 summarizes these solution concentrations and the observed buffer capacities, and Figures 5-4 through 5-11 show the buffer index plots for each acid.

TABLE 5-2. CARBOXYLIC ACID TEST SOLUTIONS

Soln #	Acid	Concentration (mM)	B_c	B_c/mM acid	Figure #
9	Acetic	17.469	5.92	0.34	5-4
10	Oxalic	11.169	3.88	0.35	5-5
11	Butyric	10.940	3.85	0.35	5-6
12	Propionic	13.404	4.52	0.34	5-7
13	Succinic	8.561	4.09	0.48	5-8
14	Glutaric	10.000	6.54	0.65	5-9
15	Malonic	10.005	4.37	0.44	5-10
16	Valeric	9.195	3.21	0.35	5-11

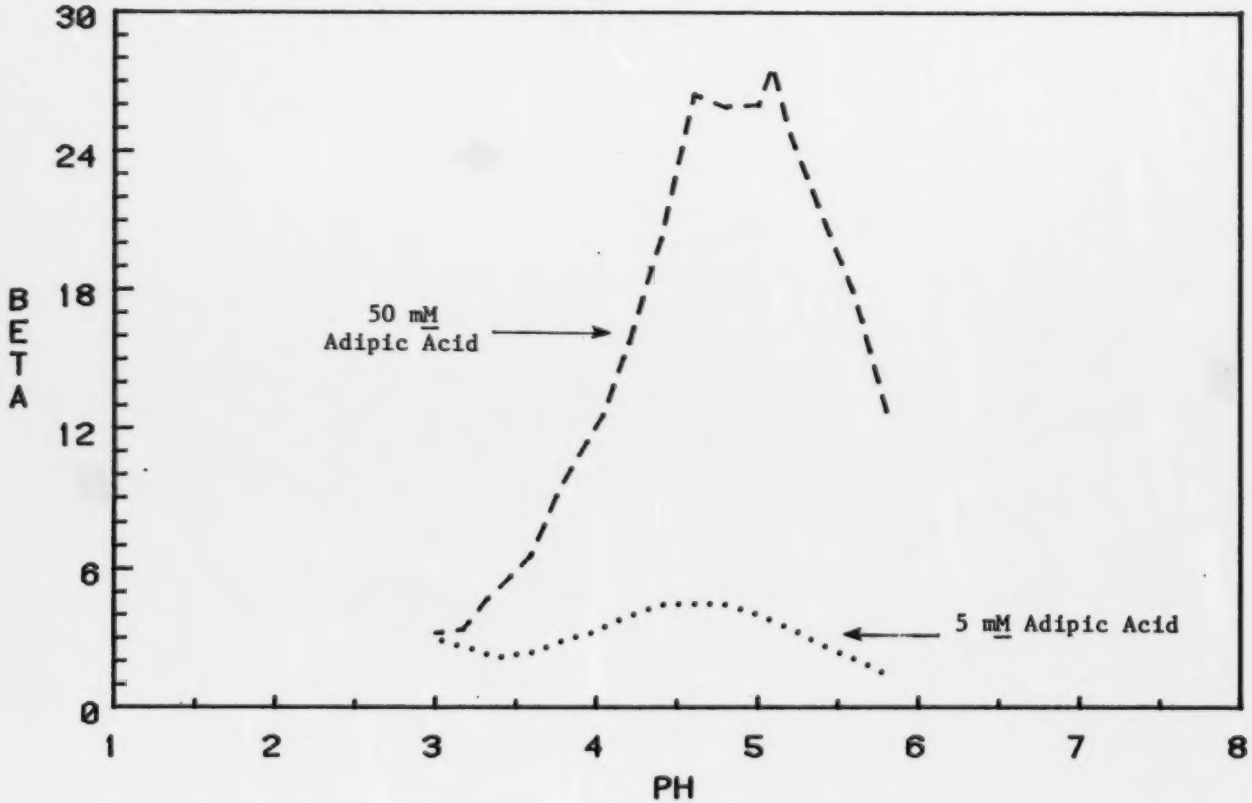


Figure 5-1. Comparison of Buffer Index Curves for Two Different Concentrations of Adipic Acid: Solution #1, 4.943 mM Adipic (dotted line); and Solution #2, 50.014 mM Adipic (dashed line)

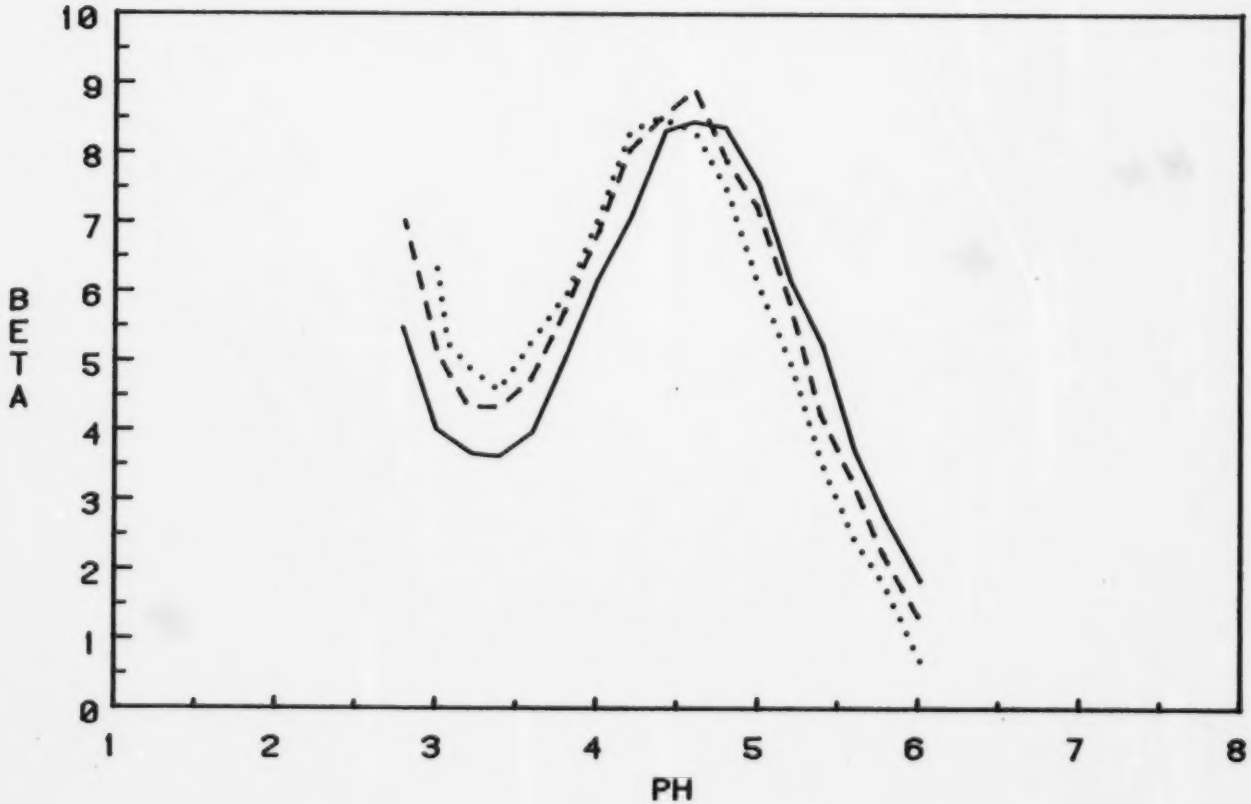


Figure 5-2. Comparison of Buffer Index Curves for 10 m$\underline{M}$ Adipic Acid Solutions at Three Ionic Strengths (μ): Solution #3, μ = 0.360 (solid line); Solution #4, μ = 0.900 (dashed line); and Solution #5, μ = 1.800 (dotted line).

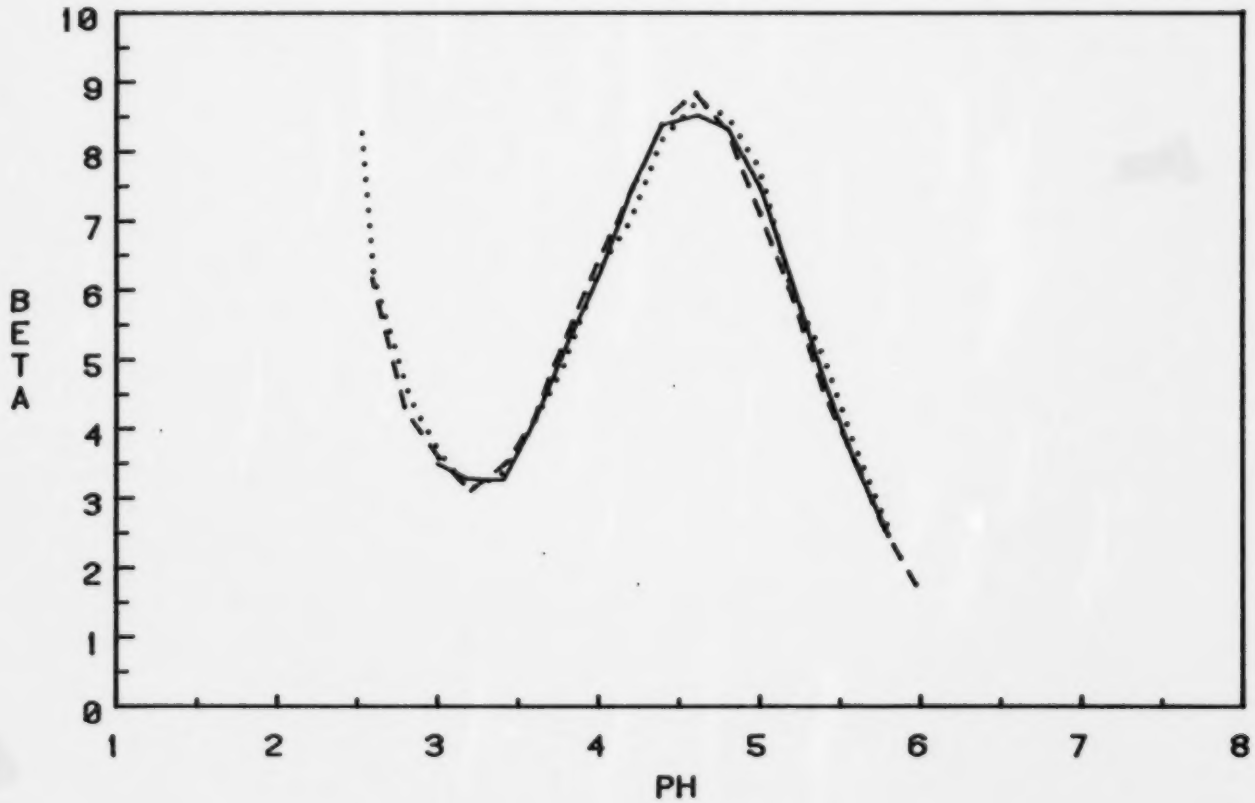


Figure 5-3. Comparison of Buffer Index Curves for 10 m$\underline{M}$ Adipic Acid Solutions Containing Varying Levels of Calcium and Magnesium: Solution #6, 70 m$\underline{M}$ Mg and no Ca (solid line); Solution #7, 50 m$\underline{M}$ Mg and 20 m$\underline{M}$ Ca (dotted line); and Solution #8, 60 m$\underline{M}$ Mg and 10 m$\underline{M}$ Ca (dashed line).

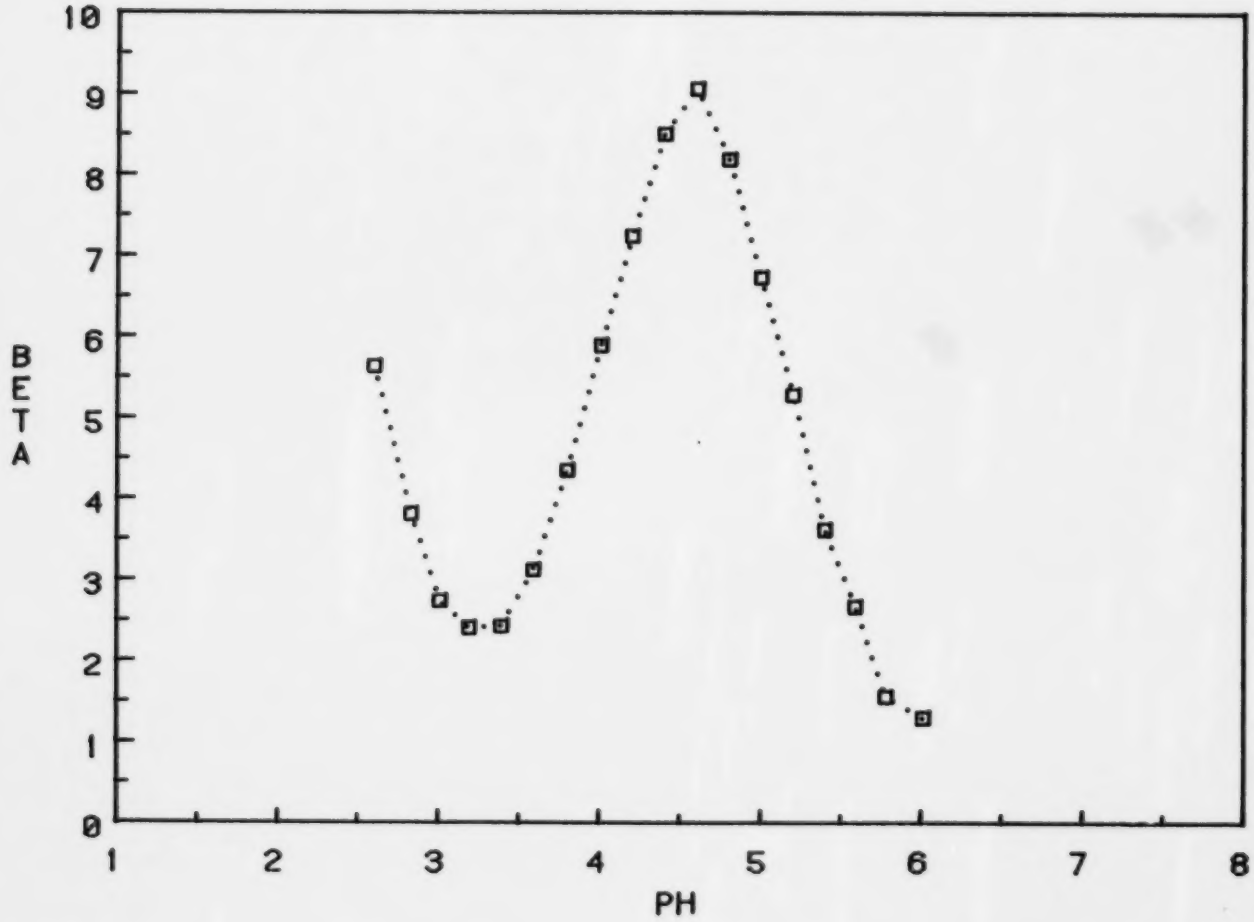


Figure 5-4. Buffer Index Curve for the Titration of 17.460 m<u>M</u> Acetic Acid

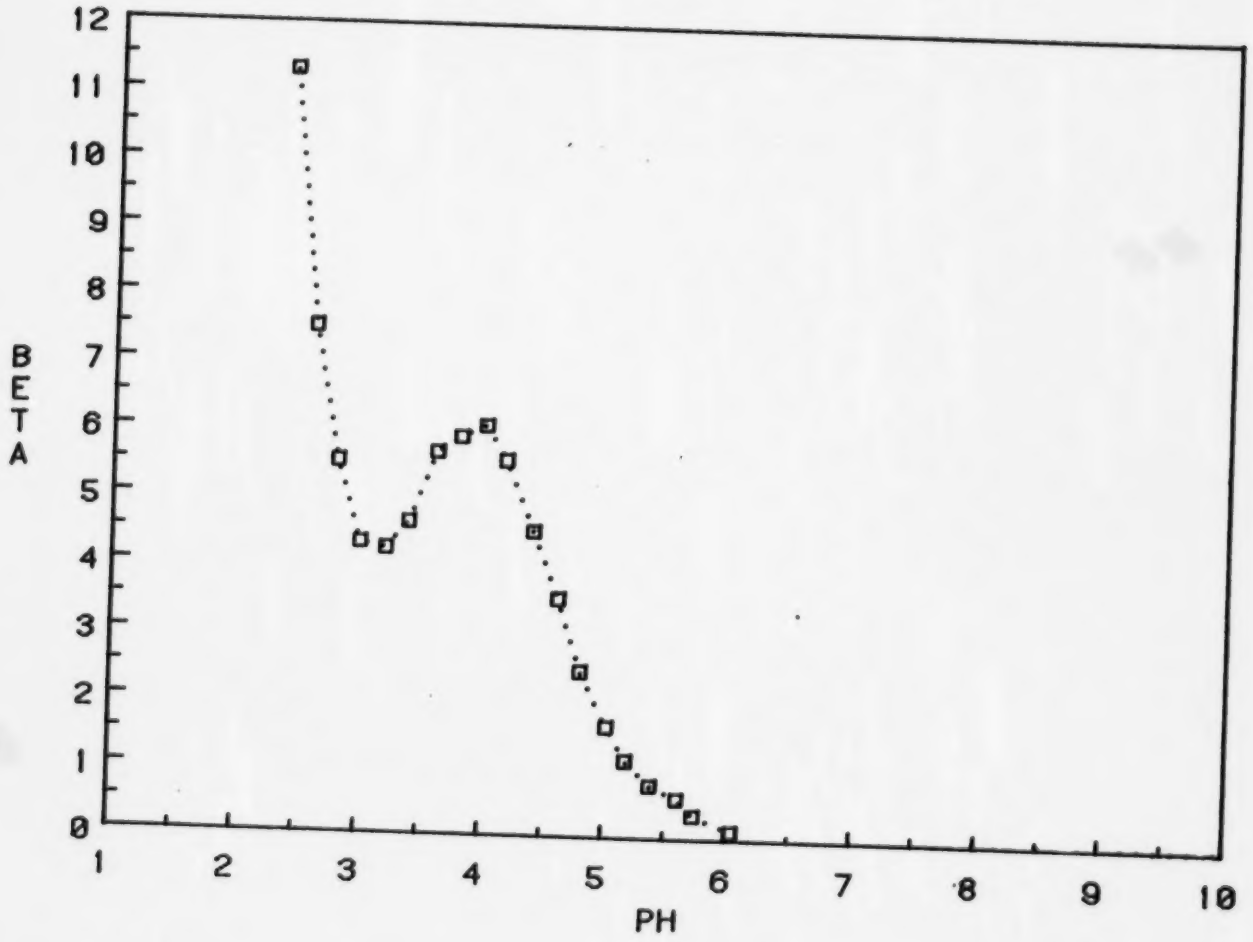


Figure 5-5. Buffer Index Curve for the Titration of 11.169 m<u>M</u> Oxalic Acid

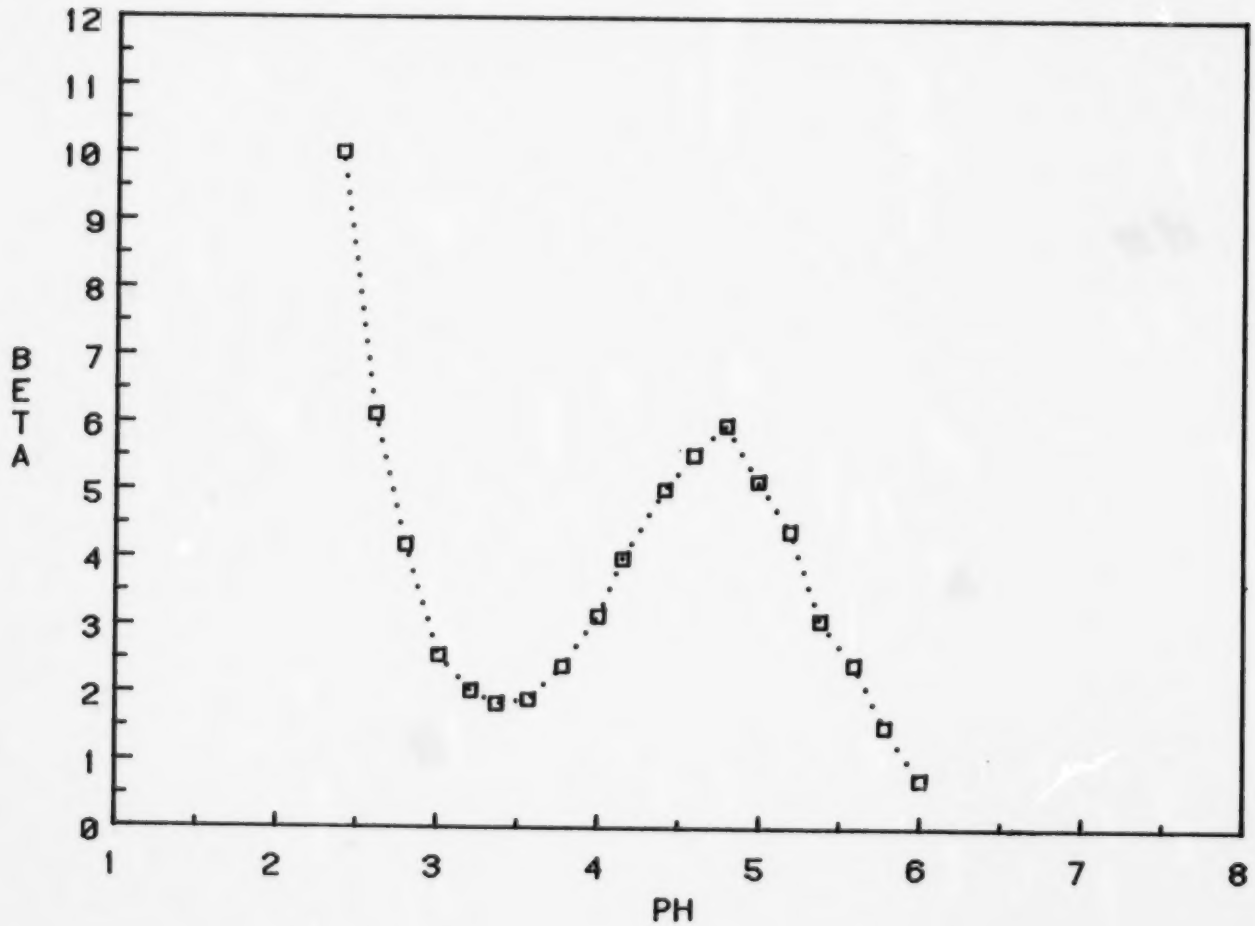


Figure 5-6. Buffer Index Curve for the Titration of 10.940 m<u>M</u> Butyric Acid

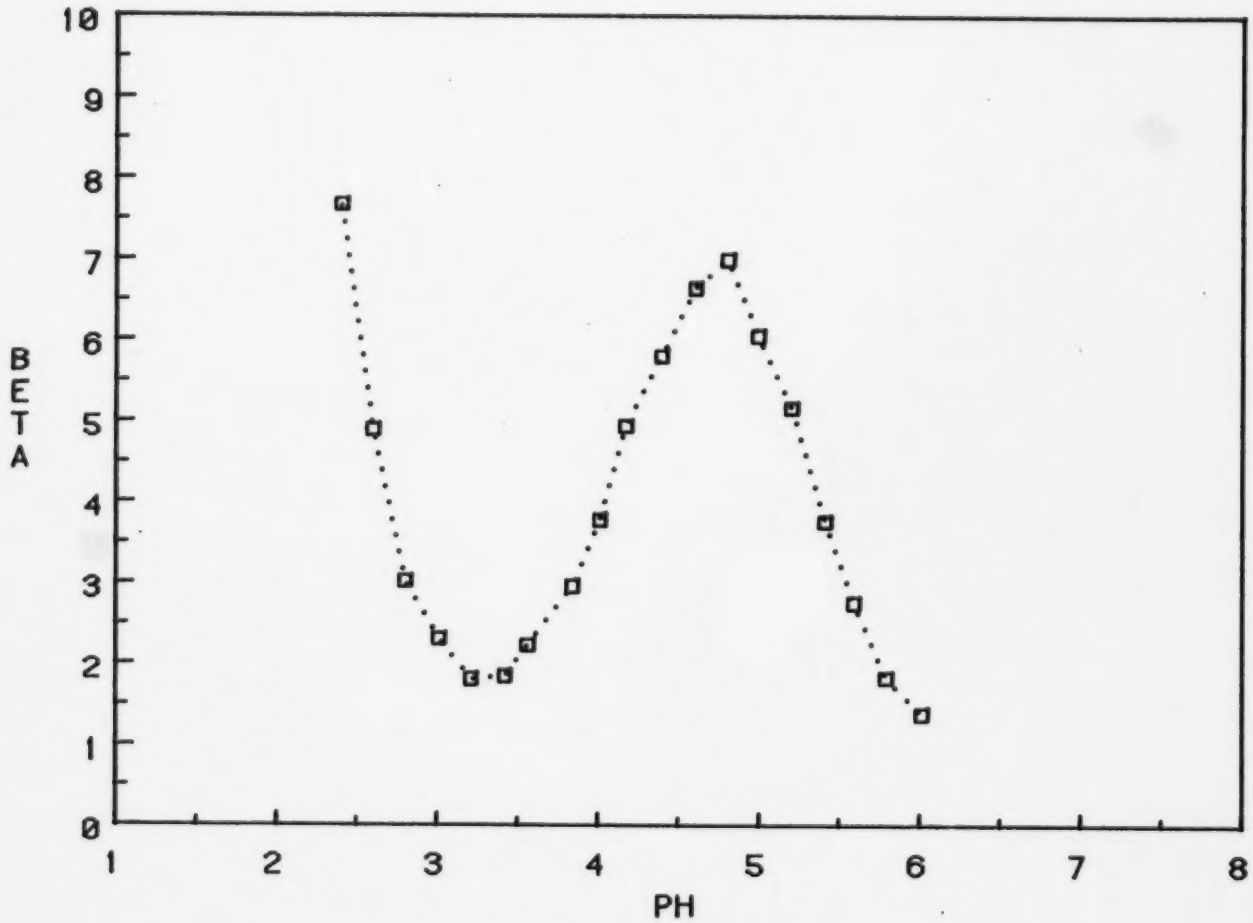


Figure 5-7. Buffer Index Curve for the Titration of 13.404 m<u>M</u> Propionic Acid

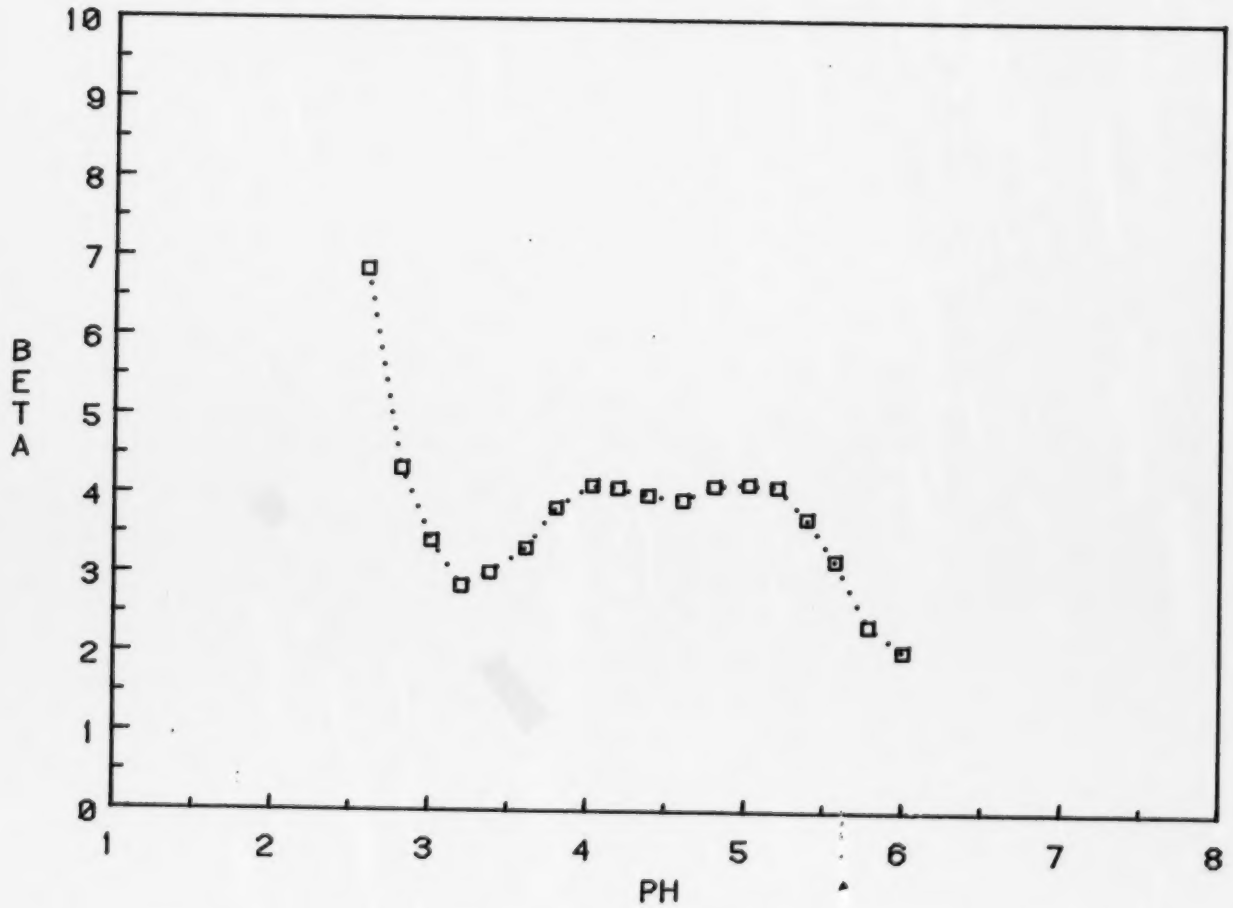


Figure 5-8. Buffer index curve for the titration of 8.561 m<u>M</u> succinic acid.

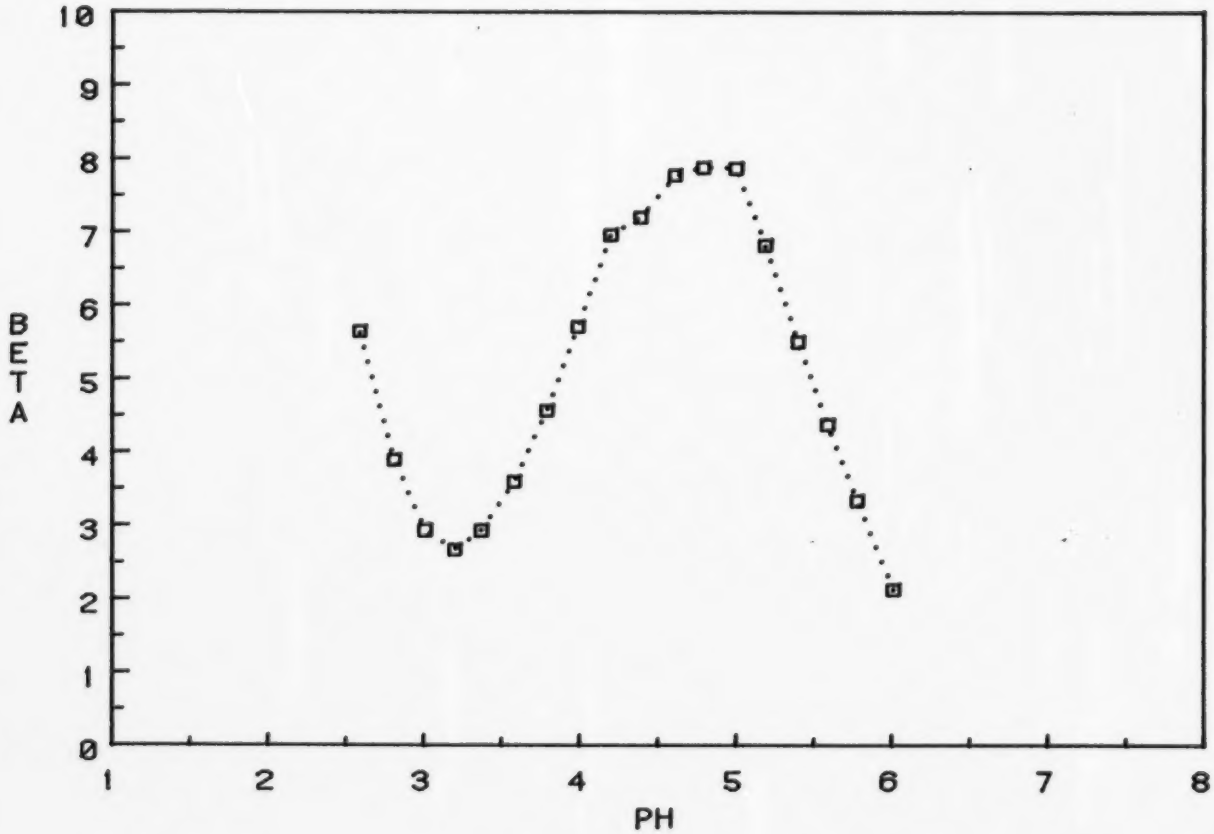


Figure 5-9. Buffer index curve for the titration of 10.000 m<u>M</u> glutaric acid.

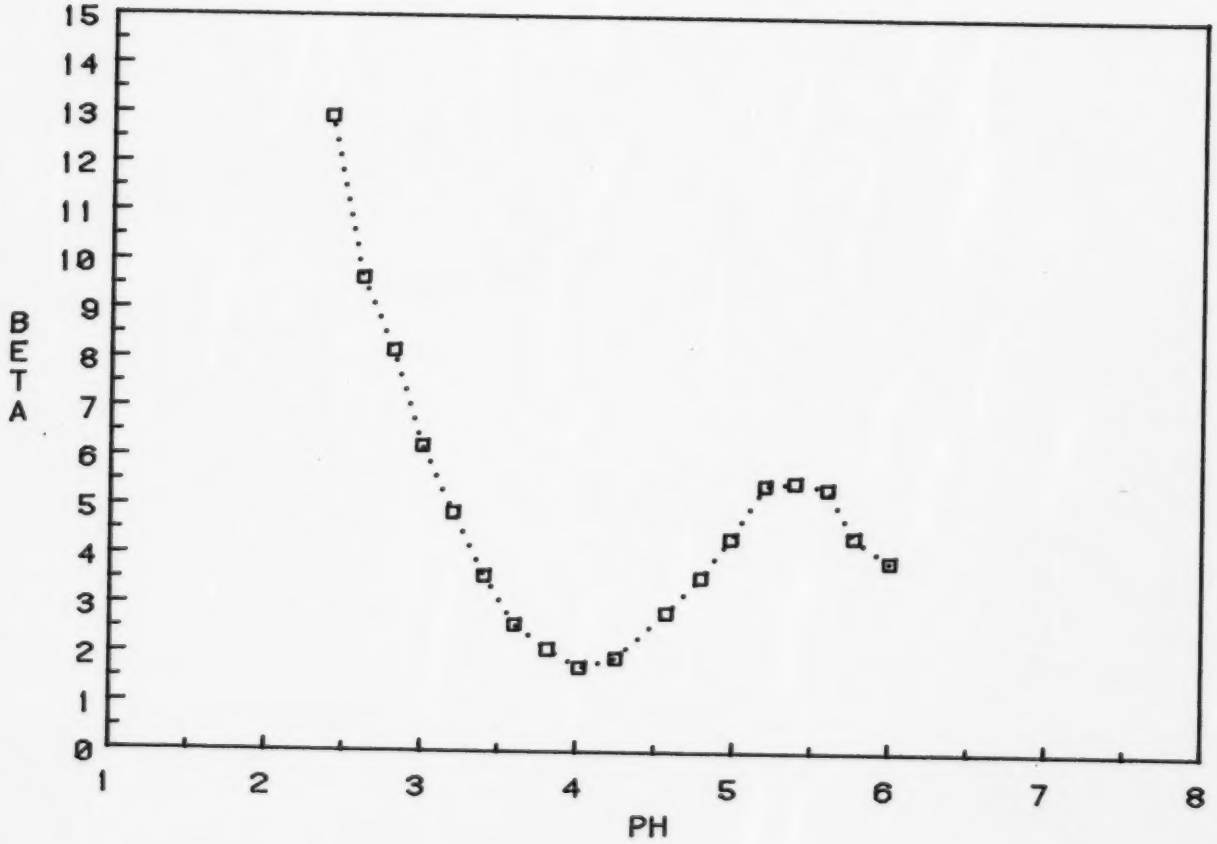


Figure 5-10. Buffer index curve for the titration of 10.005 m<u>M</u> malonic acid.

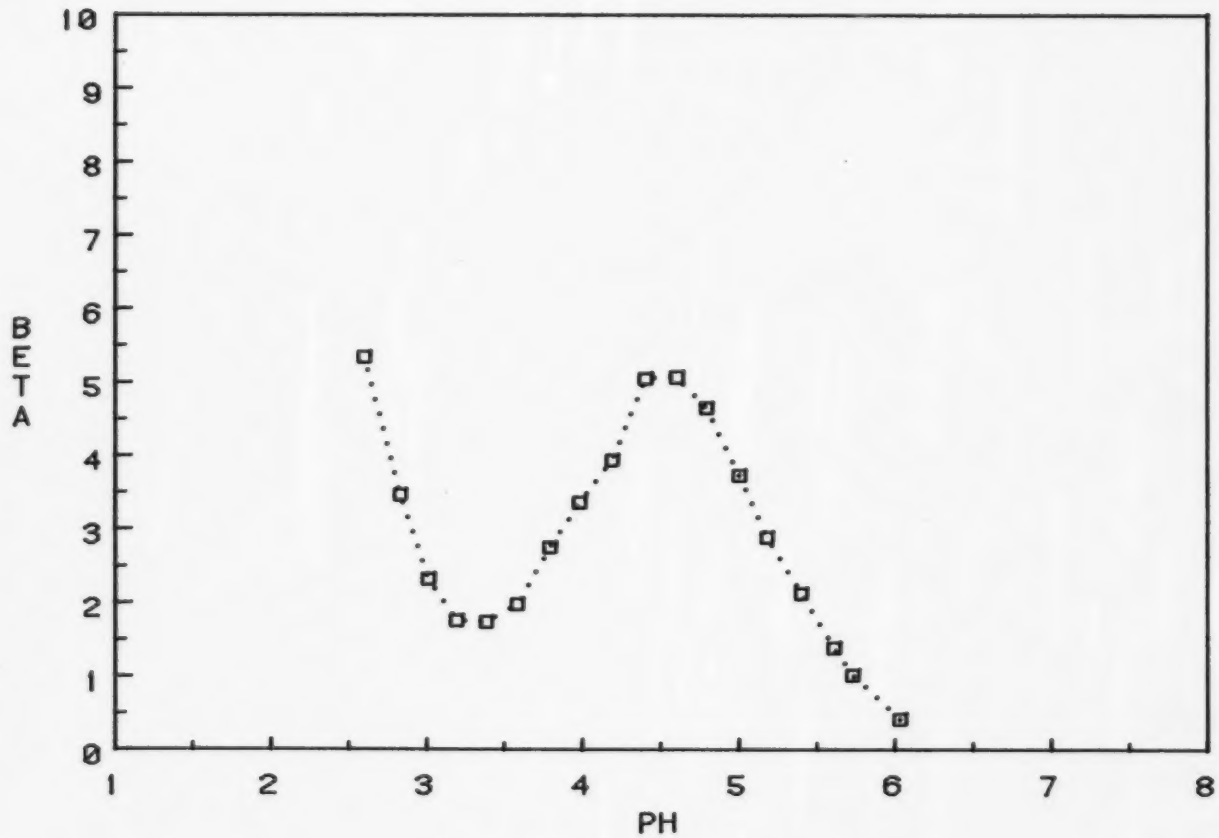


Figure 5-11. Buffer index curve for the titration of 9.195 m<u>M</u> valeric acid.

As expected, the stronger acids have β curves shifted toward lower pH's. This, in turn, is reflected in generally lower buffer capacities between pH 3-6 since the region of optimum buffering is tied to the pK's of the acids. It is interesting to note that succinic (Figure 5-8) and glutaric (Figure 5-9) exhibit pronounced double peaks due to the separation between the respective pK_1 and pK_2 values.

Finally, the combined effects of mixtures of degradation products on the buffer titration were checked using the three solutions described in Table 5-3. Performing a linear regressionon the B_c vs total normality data yields a straight line with slope = 0.365, y-intercent = -2.25, and a correlation coefficient of 1.000. Thus,

$$\text{Normality} = \frac{B_c + 2.25}{0.365}$$

Figures 5-12 through 5-14 show the respective β curves of solutions #17, #18, and #19. Aside from the obvious concentration differences, there is no pronounced effect due to the presence of degradation products.

5.2 METHOD TESTING

A practical test of the buffer titration method was provided by applying the technique to several samples of dilute filtrate from the bench-scale scrubber. Table 5-4 summarizes the results of these titrations and compares them to results obtained by GC. Normalities were calculated from buffer capacities using equation 5-1, while GC normalities represent total carboxylic acids identified by GC analyses.

Overall, the buffer titration results agree with the GC results within about ±15%. Except for run #24, the buffer capacity titration consistently yields higher normalities than GC. This trend is probably due to a combination of two factors:

1) The GC results have an estimated uncertainty of 10-20%.

2) The buffer titration measures the total weak acid concentration, which may include inorganic acids like carbonate and sulfite, and "mystery" acids not determined by GC.

Although the buffer titration cannot be used indiscriminately to estimate the adipic acid content of scrubber solutions, it should provide a reasonable measurement of total buffer capacity. If desired, a measurement more closely approximating the buffer capacity due only to organic acids can be obtained by removing carbonate and sulfite before proceeding with the buffer titration. This can be accomplished by adjusting the pH to about 2 with concentrated HCl and purging with nitrogen.

Buffer capacity titrations were used during the Adipic Acid Demonstration Program at Springfield, MO to measure and monitor adipic acid and DBA concentrations. Although, as previously stated, the buffer titration cannot measure the acid concentration on an absolute basis, the test provided a rapid, simple and reproducible means to monitor flucuations in acid concentration in the process streams. Within these limitations, the buffer titrations proved to be a very satisfactory technique to control acid addition rates and to identify process upsets.

The Adipic Acid Demonstration Program provided a unique opportunity to evaluate buffer capacity titration as a routine technique to measure buffering acid concentration in actual scrubber process samples. To this end, adipic acid concentrations were measured on thirty-nine different process samples employing both the buffer capacity titration technique and ion chromatography technique. As expected, the results of this method evaluation showed that adipic acid concentration measured by buffer titration were consistently higher than adipic acid concentration measured by ion chromatography. This is because of sulfite and carbonate present in the sample which contributes to the total buffer capacity of the sample. For buffer capacity-titration to be a usefull technique to measure acid concentration in scrubber samples, the contribution of other buffering species would have to be constant. This was found to be

true for the samples evaluated at Springfield. The percent difference for the samples evaluated ranged from (+16) to (+25). The mean percent difference and standard deviation of percent difference were 21 and 2.9 respectively.

TABLE 5-3. DEGRADATION PRODUCT TEST SOLUTIONS

Acid	Acid Concentrations (mM)		
	Solution #17	Solution #18	Solution #19
Acetic	0.070	0.070	0.070
Oxalic	0.089	0.089	0.089
Propionic	1.019	1.019	1.019
Butyric	1.006	1.006	1.006
Malonic	1.201	1.201	1.201
Succinic	0.993	0.993	0.993
Valeric	4.965	4.965	4.965
Glutaric	5.000	5.000	5.000
Adipic	5.200	10.000	48.000
Total Normality mea/l	32.026	41.626	117.626
Buffer Capacity B_c	9.73	12.64	40.76

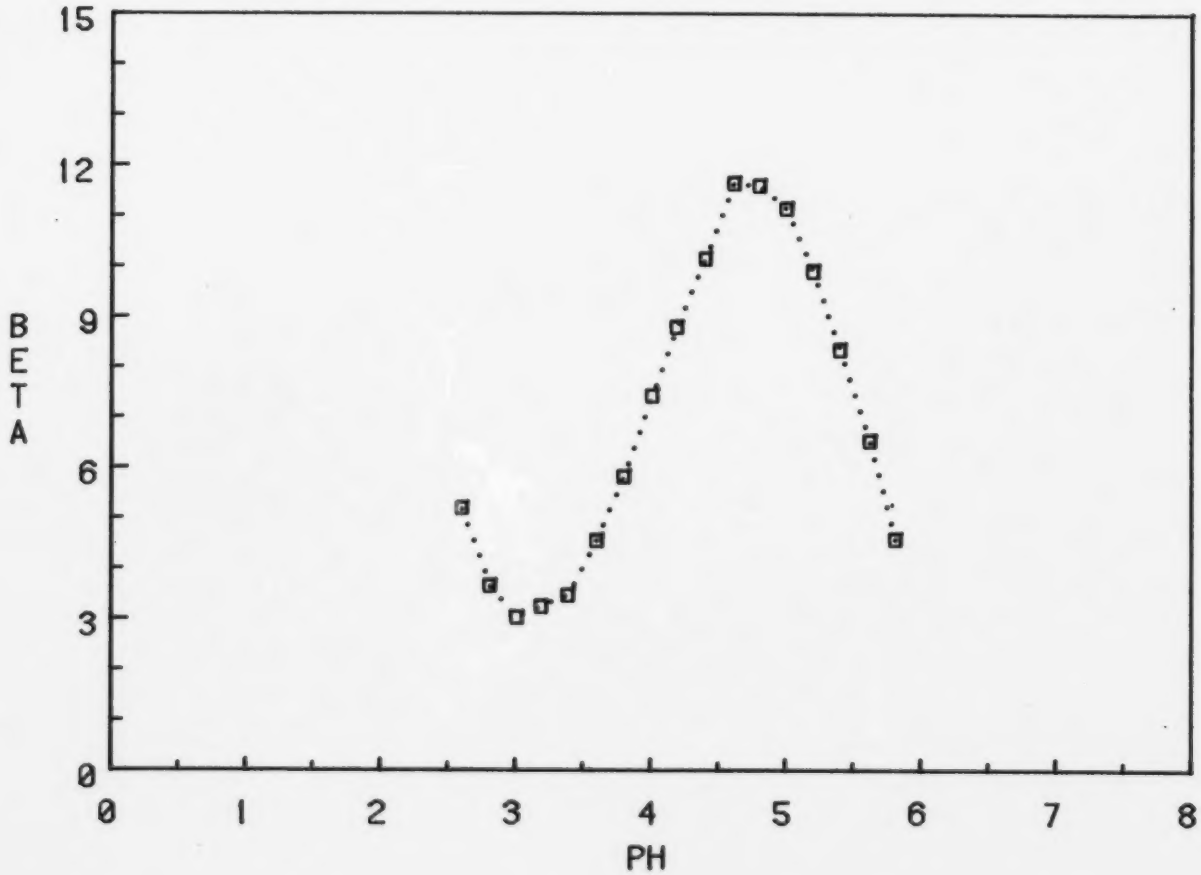


Figure 5-12. Buffer index curve for a 0.032 N mixture of nine carboxylic acids (Solution #17).

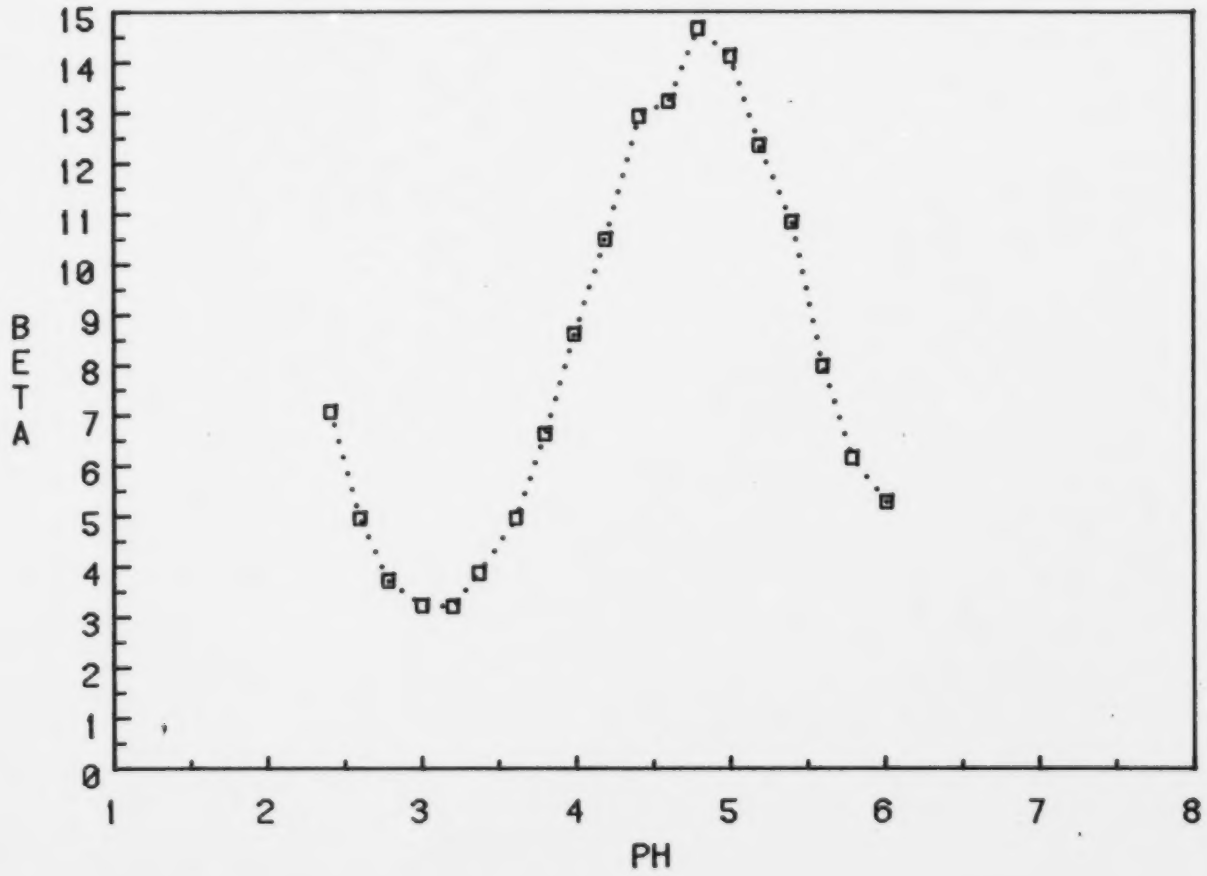


Figure 5-13. Buffer index curve for a 0.042 N mixture of nine carboxylic acids (Solution #18).

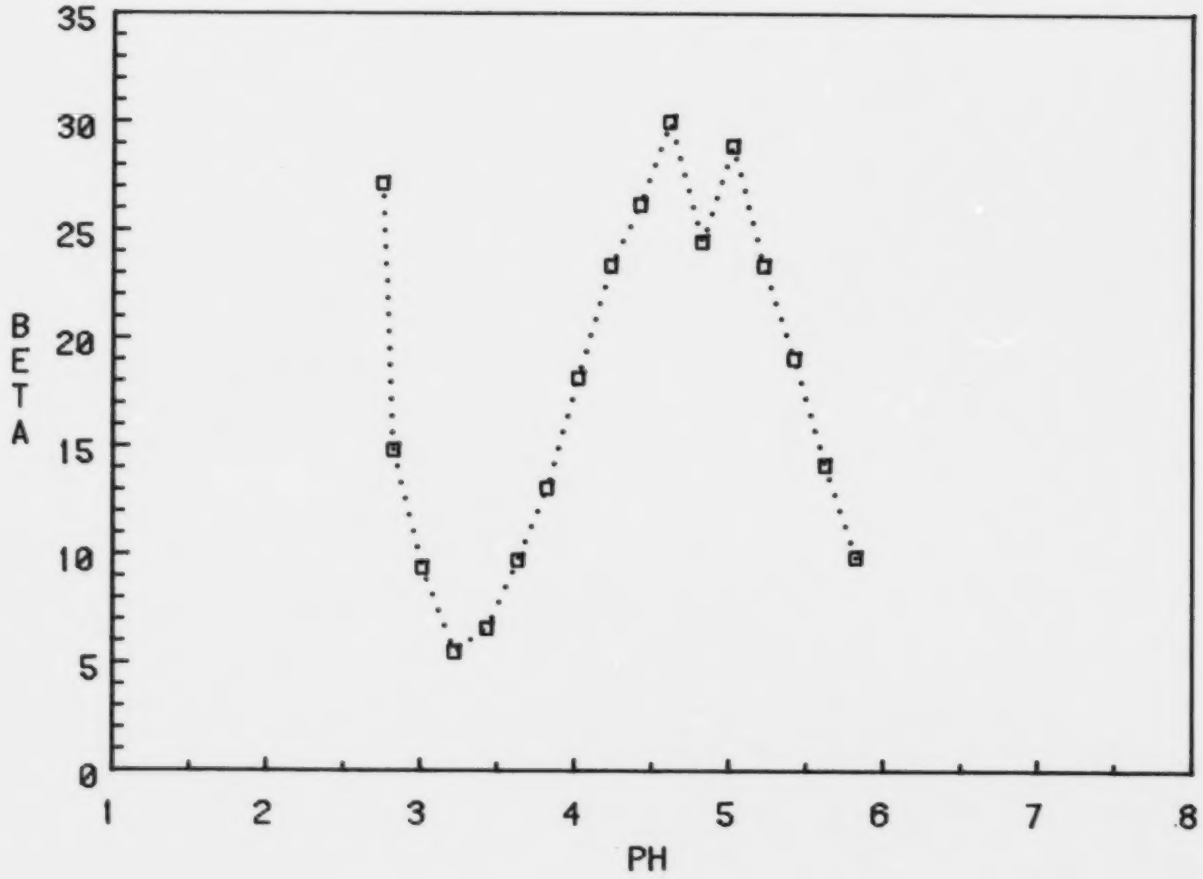


Figure 5-14. Buffer index curve for a 0.118 N mixture of nine carboxylic acids (Solution #19).

TABLE 5-4. BUFFER CAPACITIES OF FILTRATES FROM SEVERAL BENCH-SCALE SCRUBBER RUNS

Run #	B_c	Dilution Factor	Corrected[a] B_c	Total Normality (meg/l) by B_c	by GC	% Δ[b]
17	7.44	2.35	17.5	54.4	48.1	+13
19	6.10	2.40	14.7	45.3	39.4	+15
23	3.00	2.17	6.5	18.7	17.7	+6
24	16.87	2.11	35.5	112.9	131.1	-14
25	9.38	2.21	20.8	65.1	44.5	+46
27	7.26	2.31	16.8	52.1	43.9	+19

[a]Corrected $B_c = B_c \times$ (Dilution Factor)

[b]% Δ = [(Normality by B_c) - (Normality by GC)]/(Normality by GC)

APPENDIX C

PROCESS AND ANALYTICAL DATA PLOTS

APPENDIX C

PROCESS AND ANALYTICAL DATA PLOTS

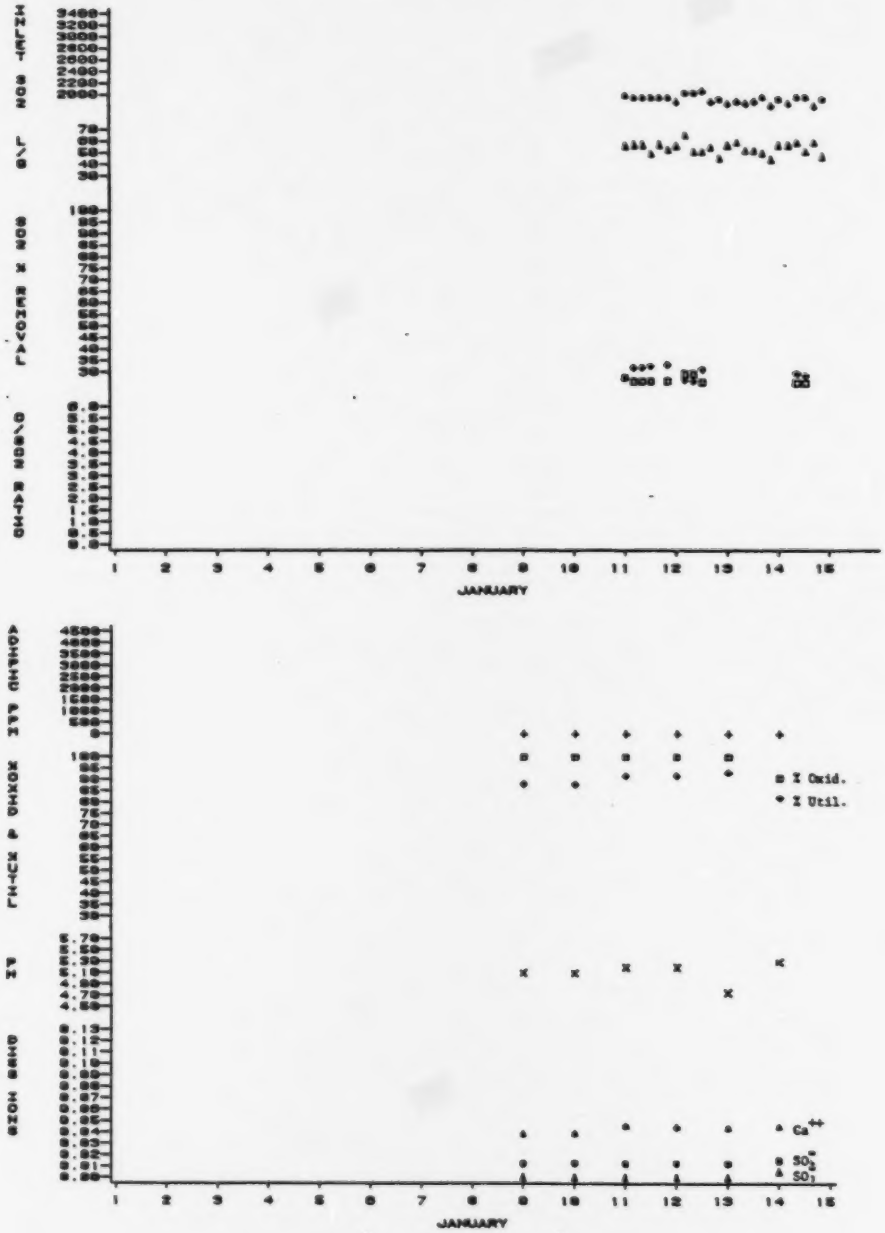
The following figures present important process and analytical data collected throughout the program. The data is plotted against time and each figure contains two weeks of information. The points that are plotted are actual measurements and not averages.

For the forced oxidation test period, January through April, 1981, the following information is presented:

- Scrubber Inlet SO_2, ppm dry
- Scrubber Liquid-to-Gas Ratio, gal/10^3 acf
- SO_2 Removal, percent dry
- O/SO_2 Ratio, lb-atoms oxygen/lb-mole SO_2 absorbed
- Adipic Acid Concentration, ppm
- Sulfite Oxidation, mole percent
- Limestone Utilization, percent
- Scrubber Feed pH
- Scrubber Feed Dissolved Ion Concentration (Ca, SO_3, SO_4), g-moles/ℓ

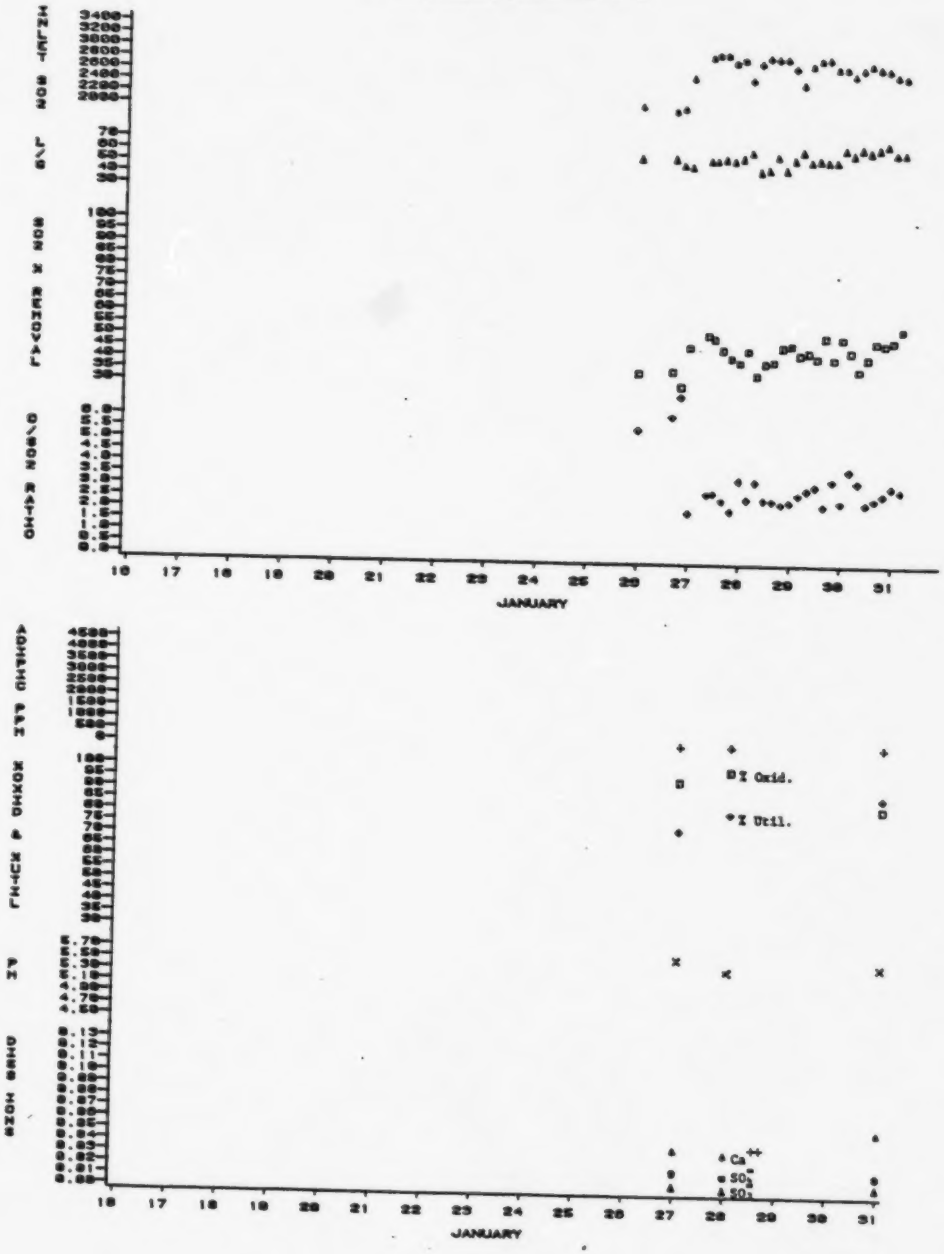
For the natural oxidation test period, May to October, 1981, the same information is presented except O/SO_2 ratio. During the DBA testing in September and October, the DBA liquid phase concentration in the scrubber feed is reported as equivalent adipic acid.

SCRUBBER MODULE S-1



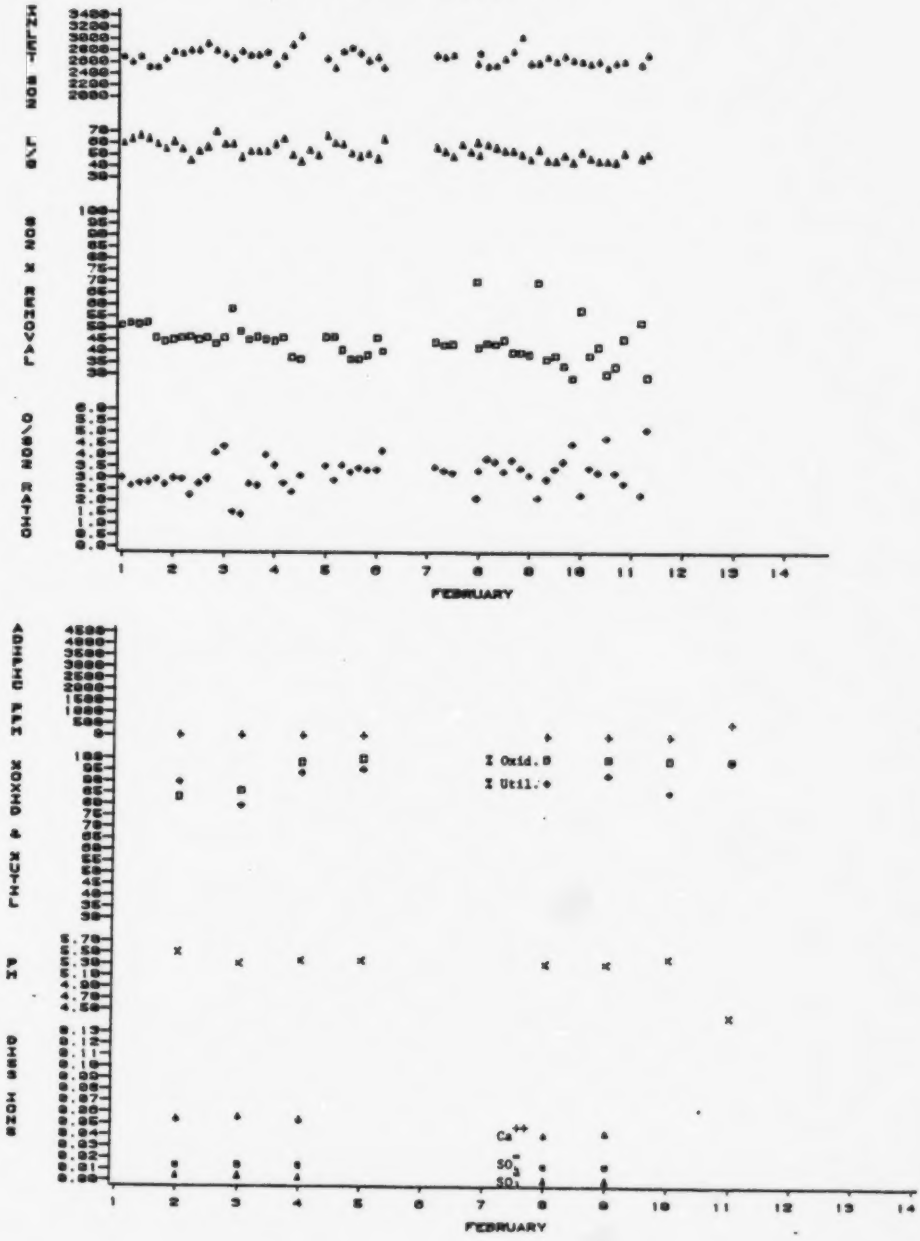
Module S-1 - Forced Oxidation (Baseline - No TCA Spheres)

SCRUBBER MODULE S-1



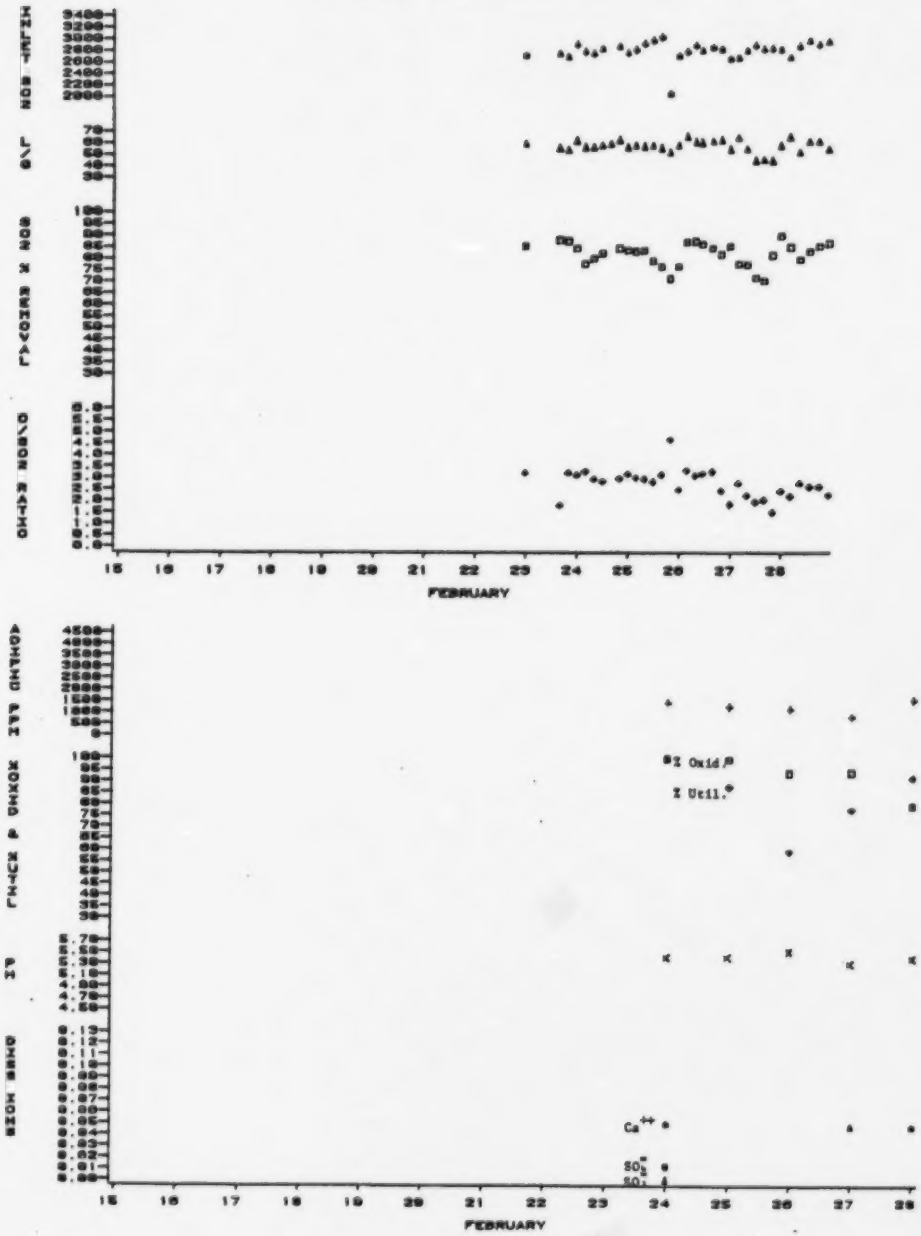
Module S-1 - Forced Oxidation (Baseline - No TCA Spheres)

SCRUBBER MODULE S-1



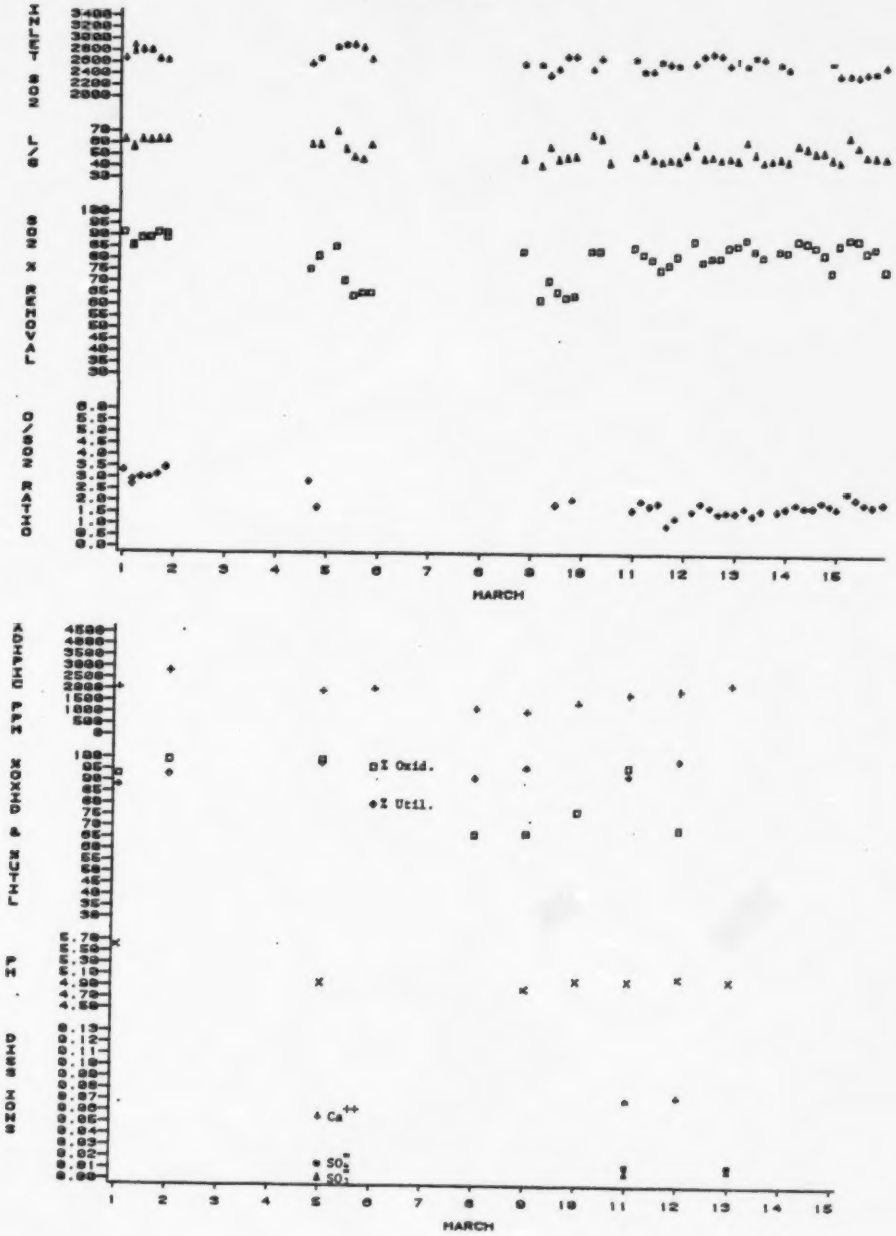
Module 1 - Forced Oxidation (Baseline - No TCA Spheres)

SCRUBBER MODULE S-1



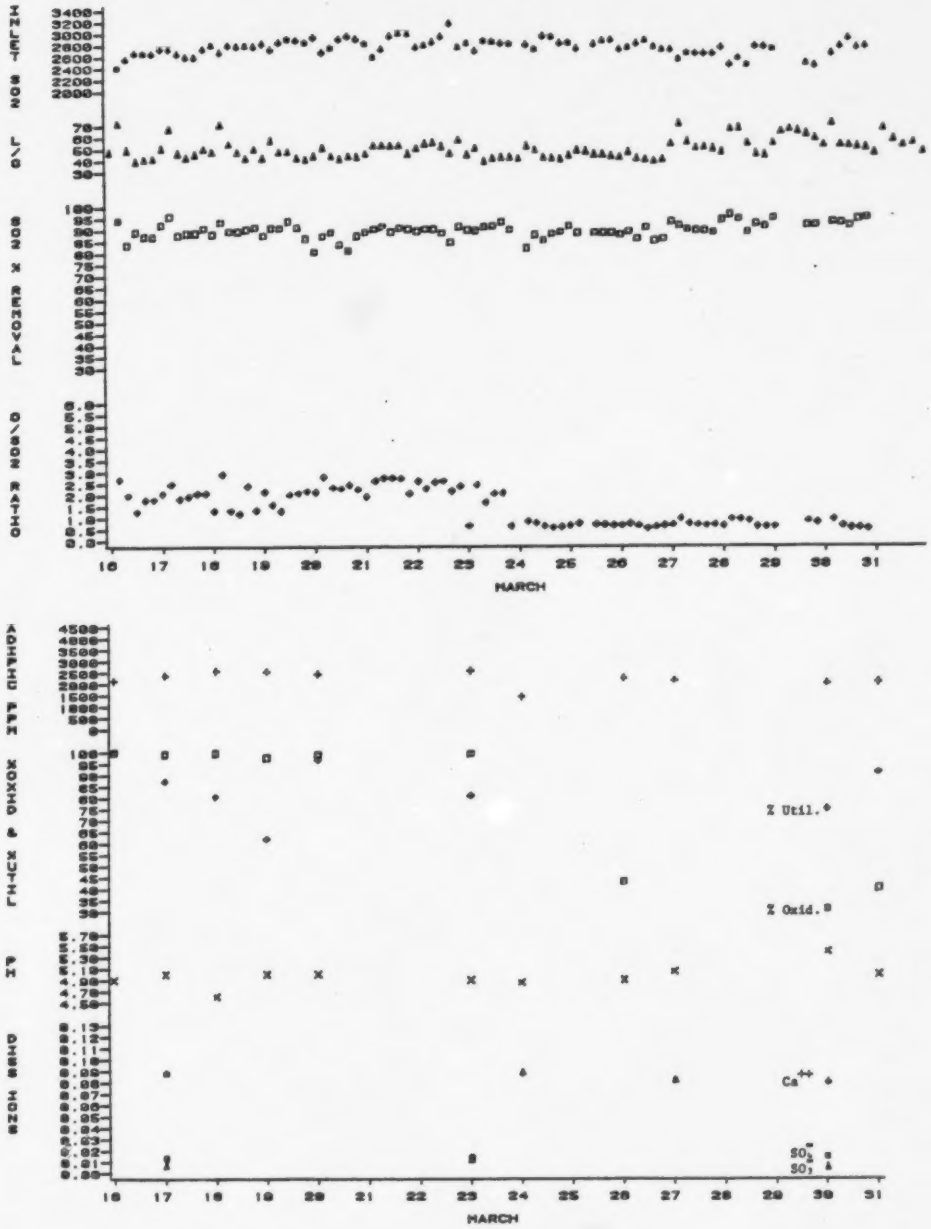
Module S-1 - Forced Oxidation (Adipic Acid - No TCA Spheres)

SCRUBBER MODULE S-1



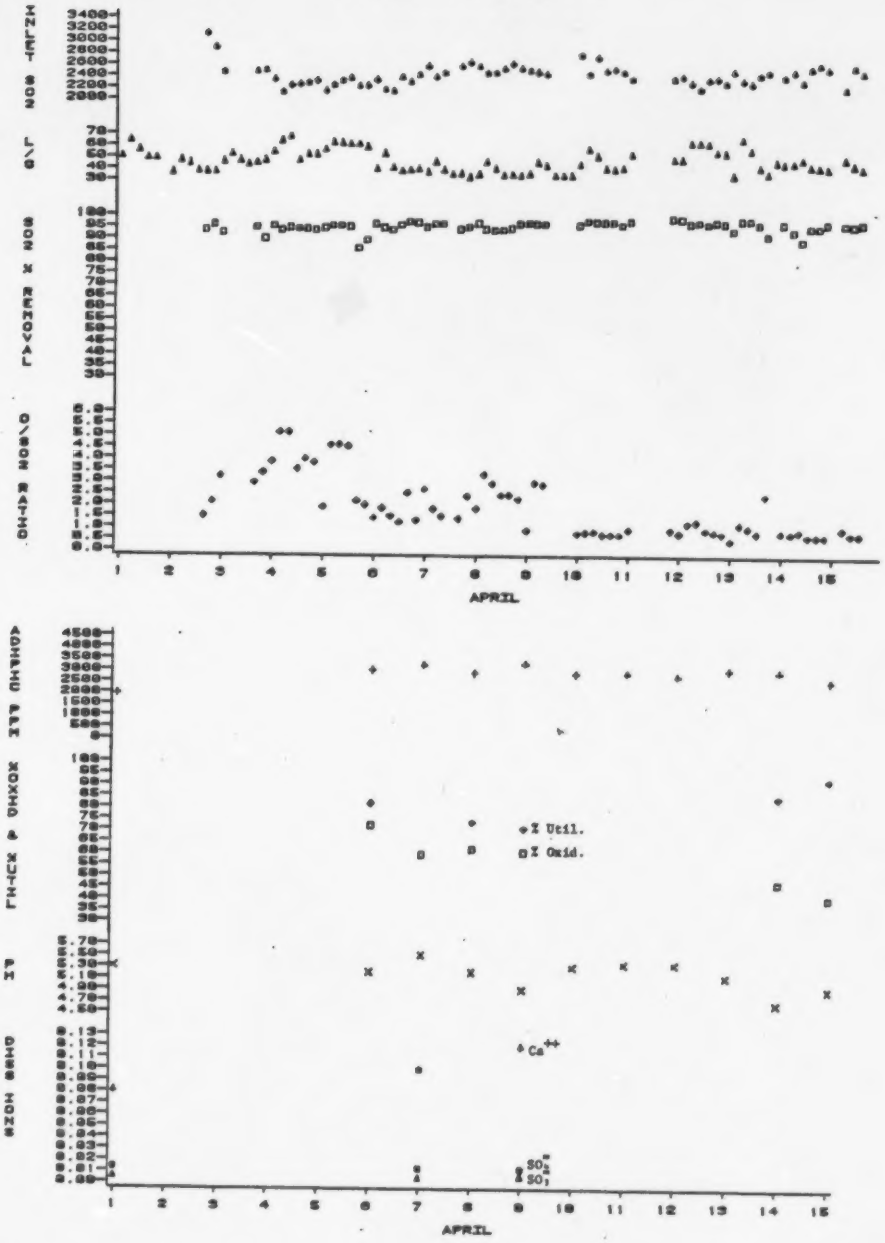
Module S-1 - Forced Oxidation (Adipic Acid)

SCRUBBER MODULE S-1



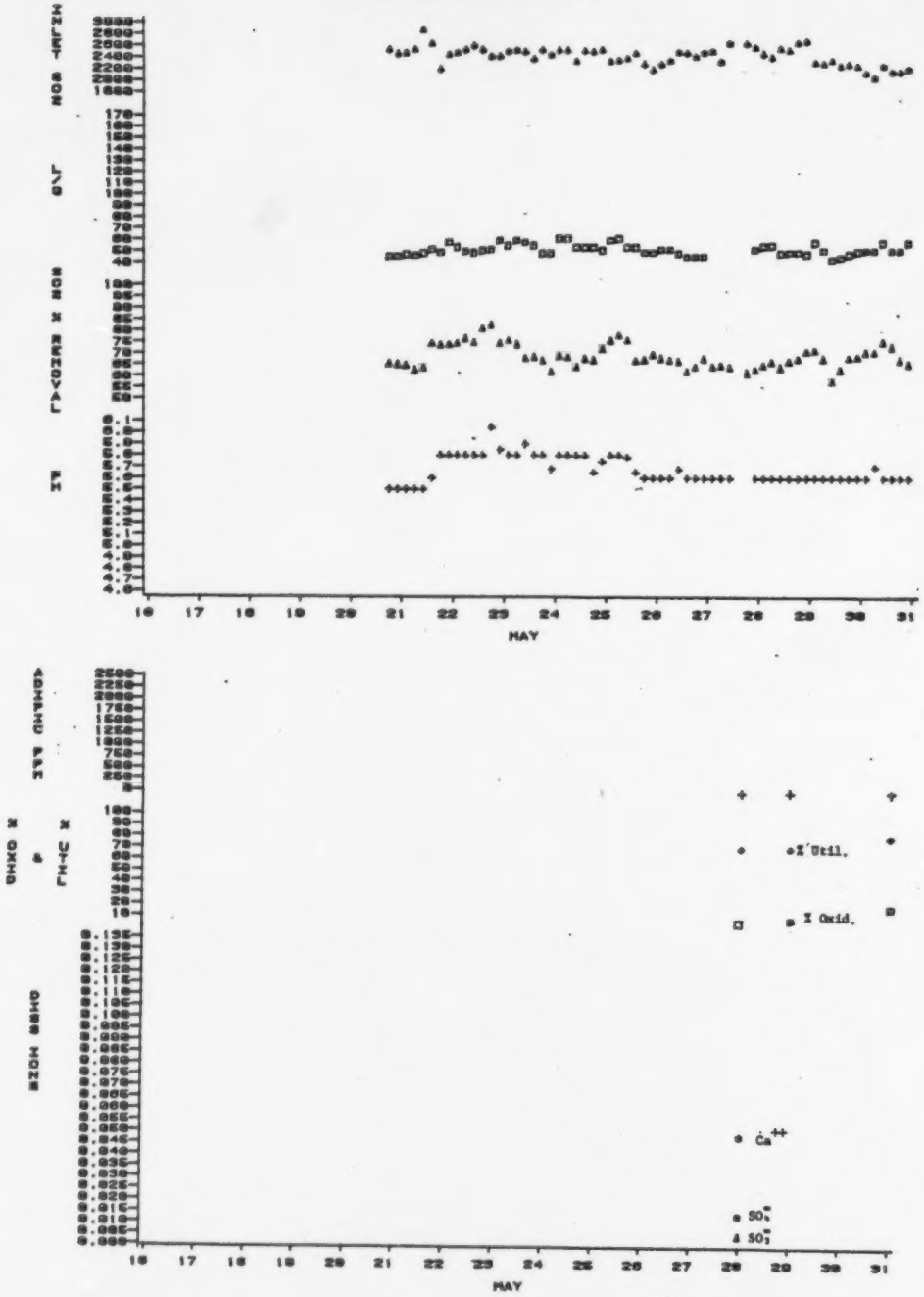
Module S-1 - Forced Oxidation (Adipic Acid)

SCRUBBER MODULE S-1



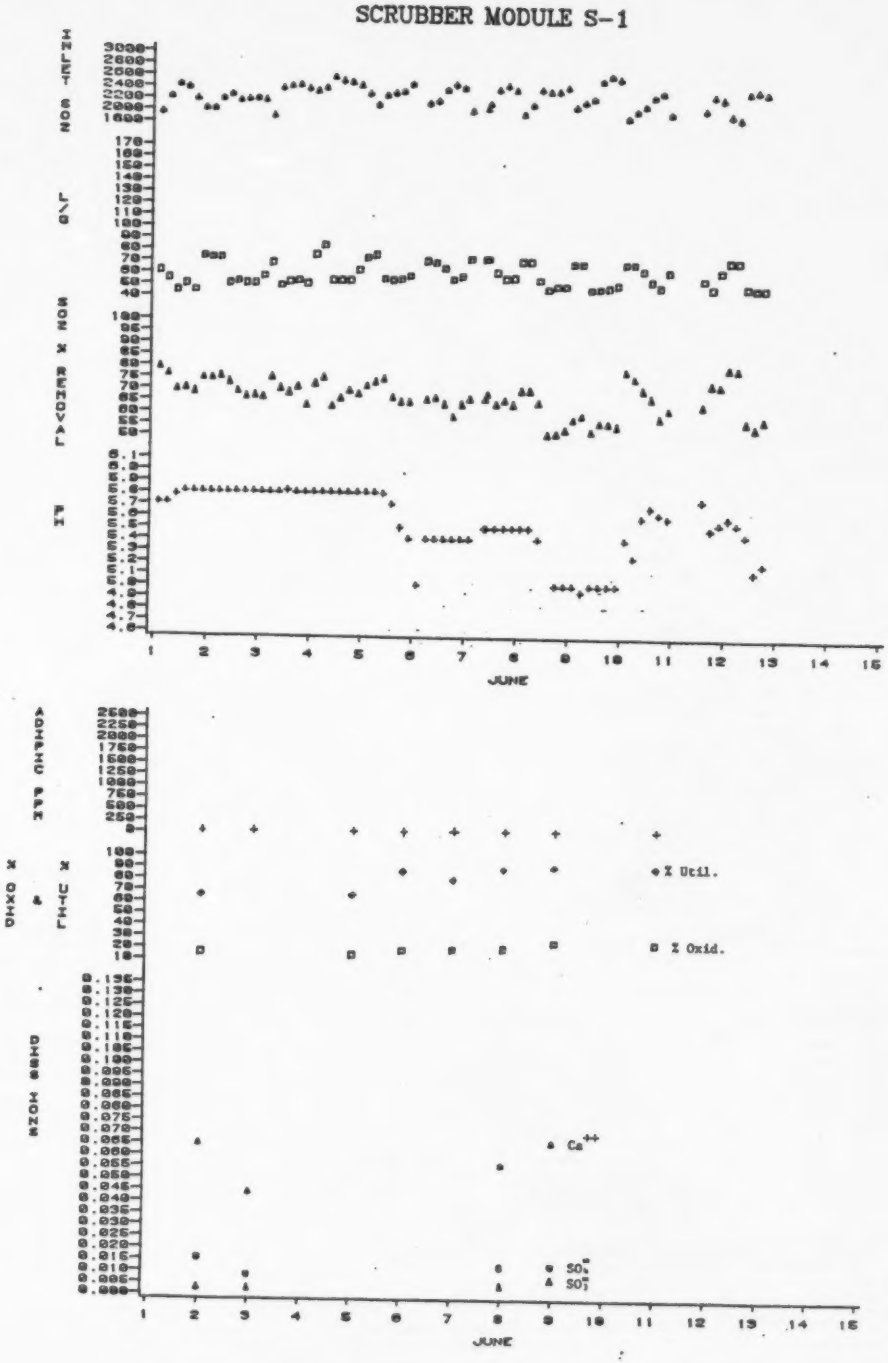
Moduel S-1 - Forced Oxidation (Adipic Acid)

SCRUBBER MODULE S-1



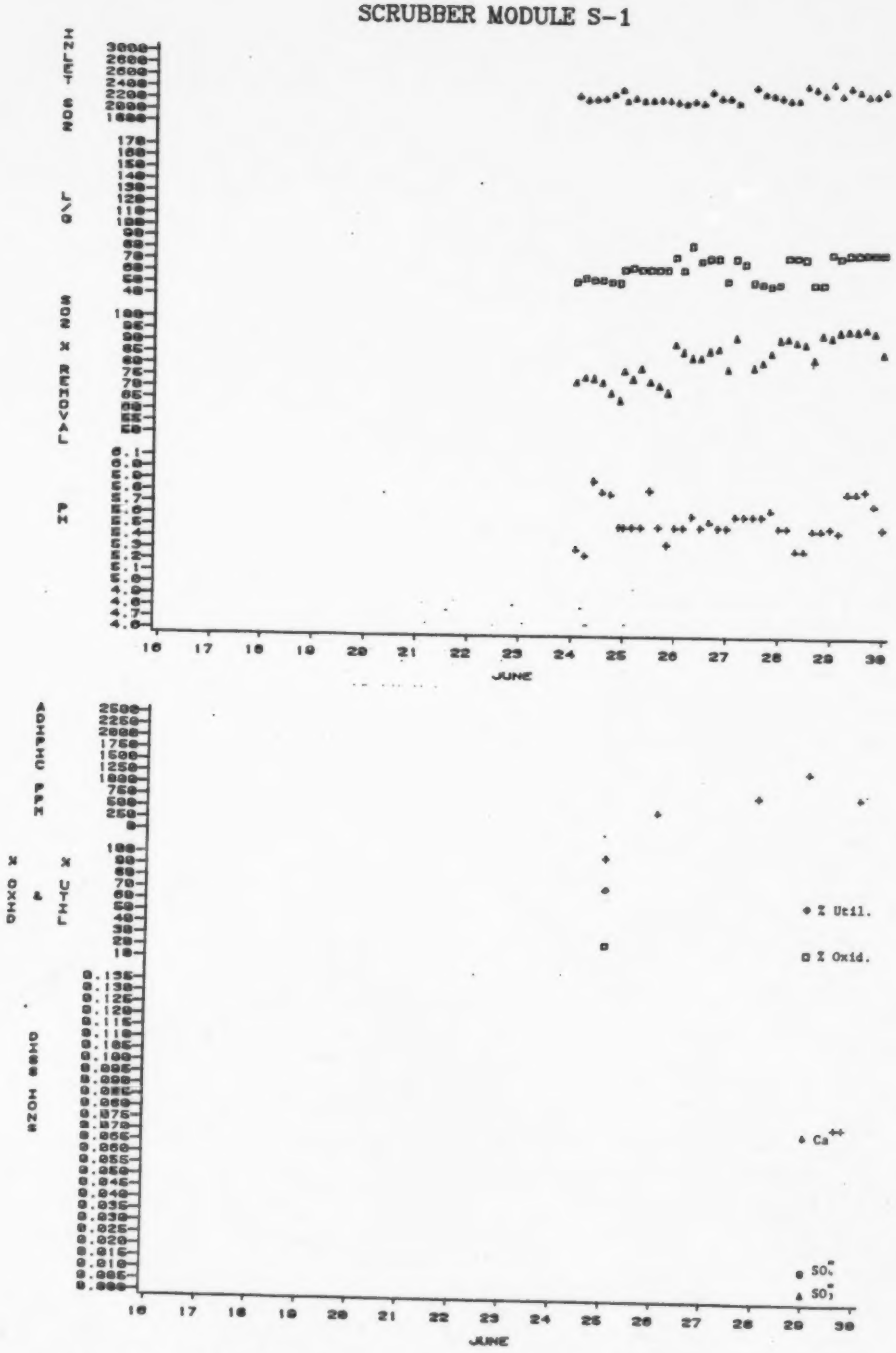
Module S-1 (Tray Tower) - Natural Oxidation (Baseline)

SCRUBBER MODULE S-1



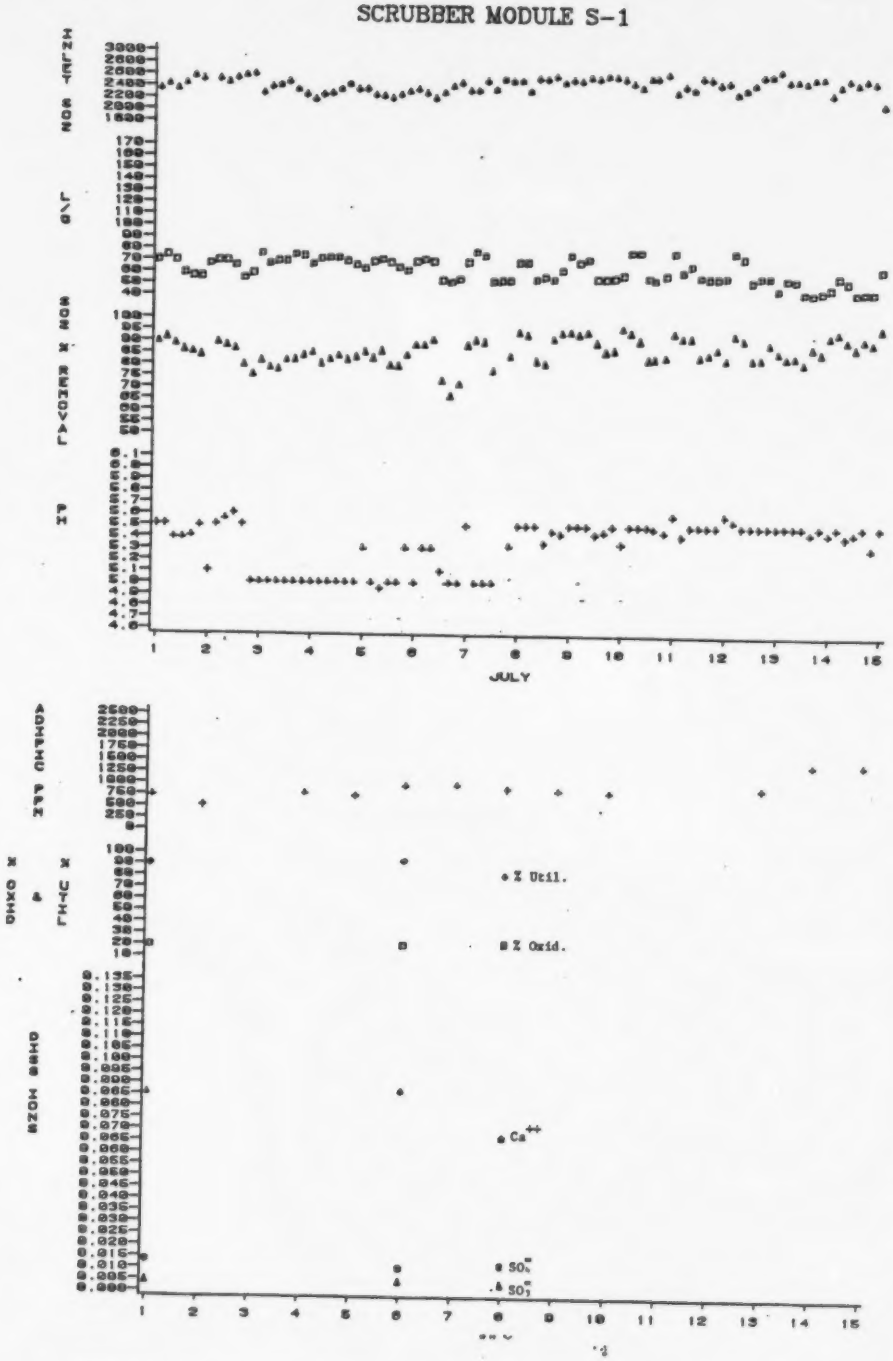
Module S-1 (Tray Tower) - Natural Oxidation (Baseline)

SCRUBBER MODULE S-1



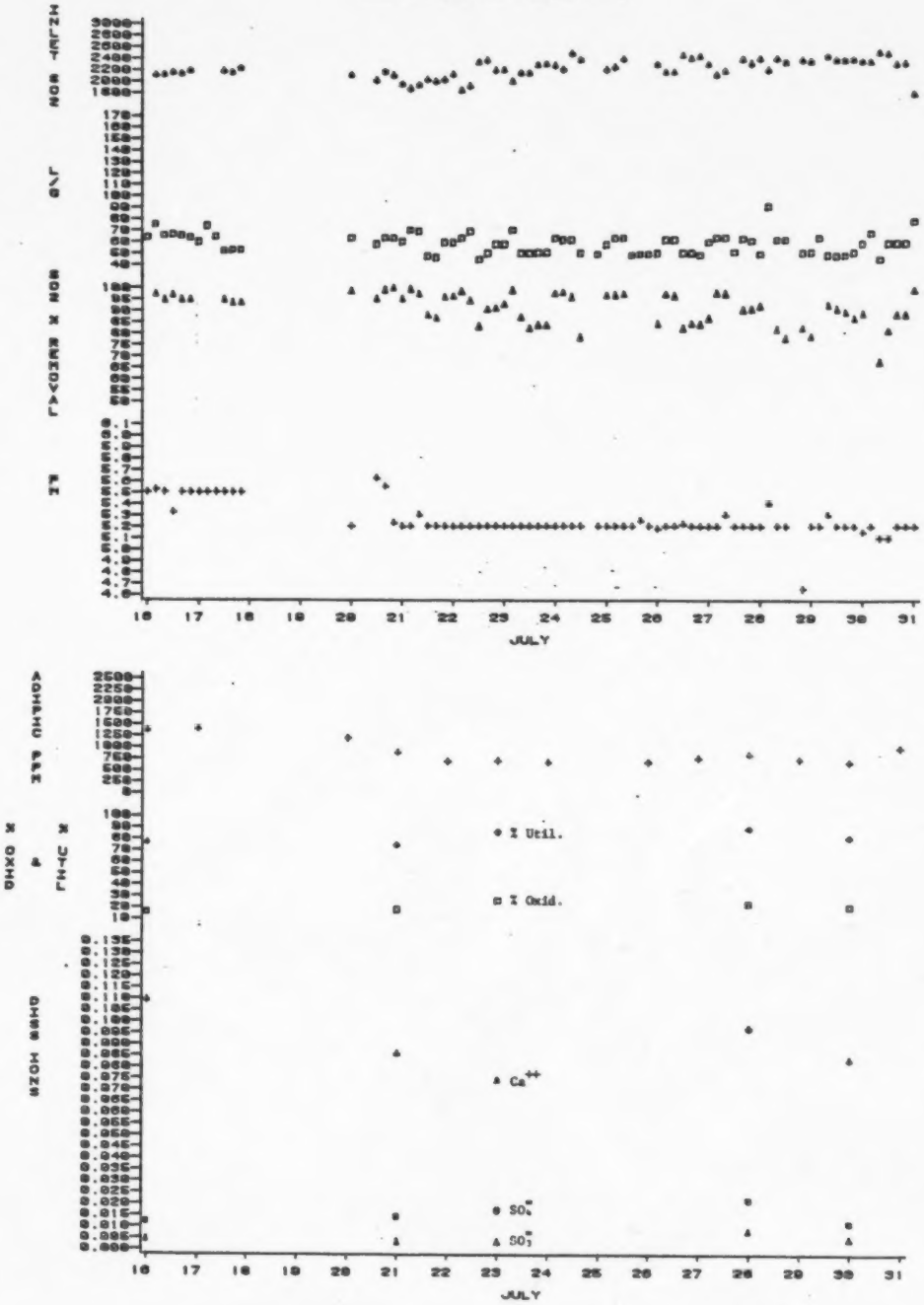
Moduel S-1 (Tray Tower) - Natural Oxidation (Adipic Acid)

SCRUBBER MODULE S-1



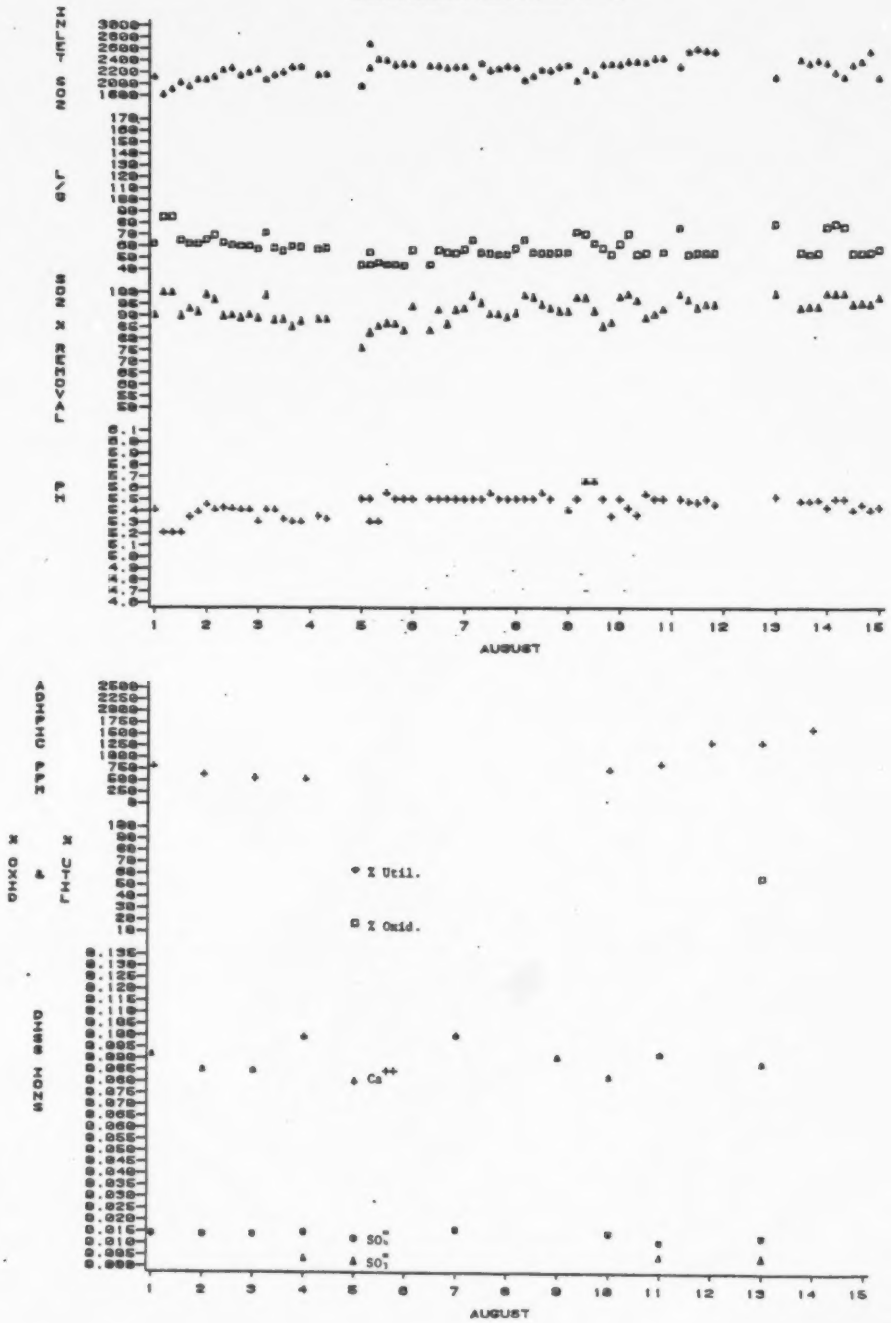
Module S-1 (Tray Tower) - Natural Oxidation (Adipic Acid)

SCRUBBER MODULE S-1



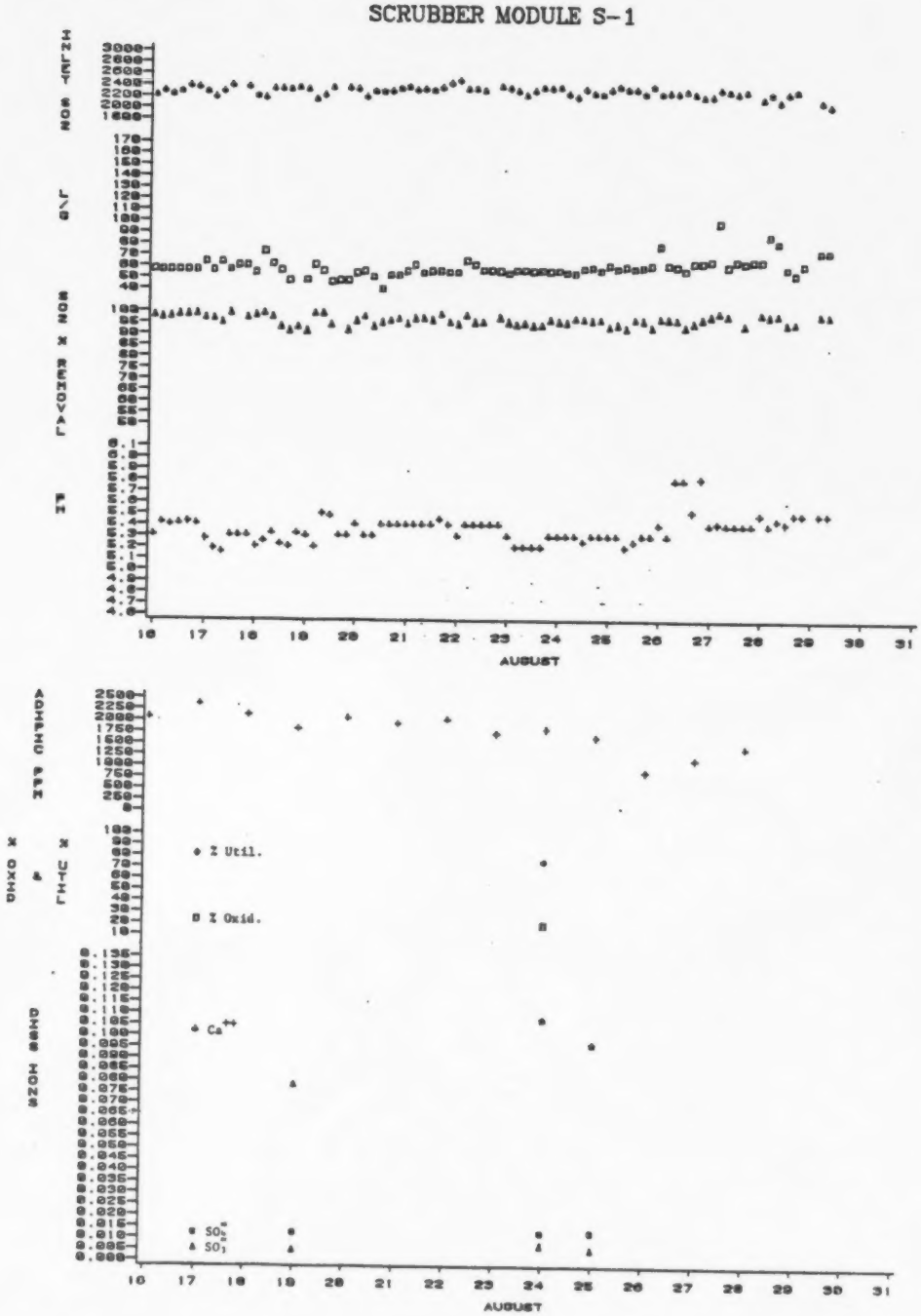
Module S-1 (Tray Tower) - Natural Oxidation (Adipic Acid)

SCRUBBER MODULE S-1



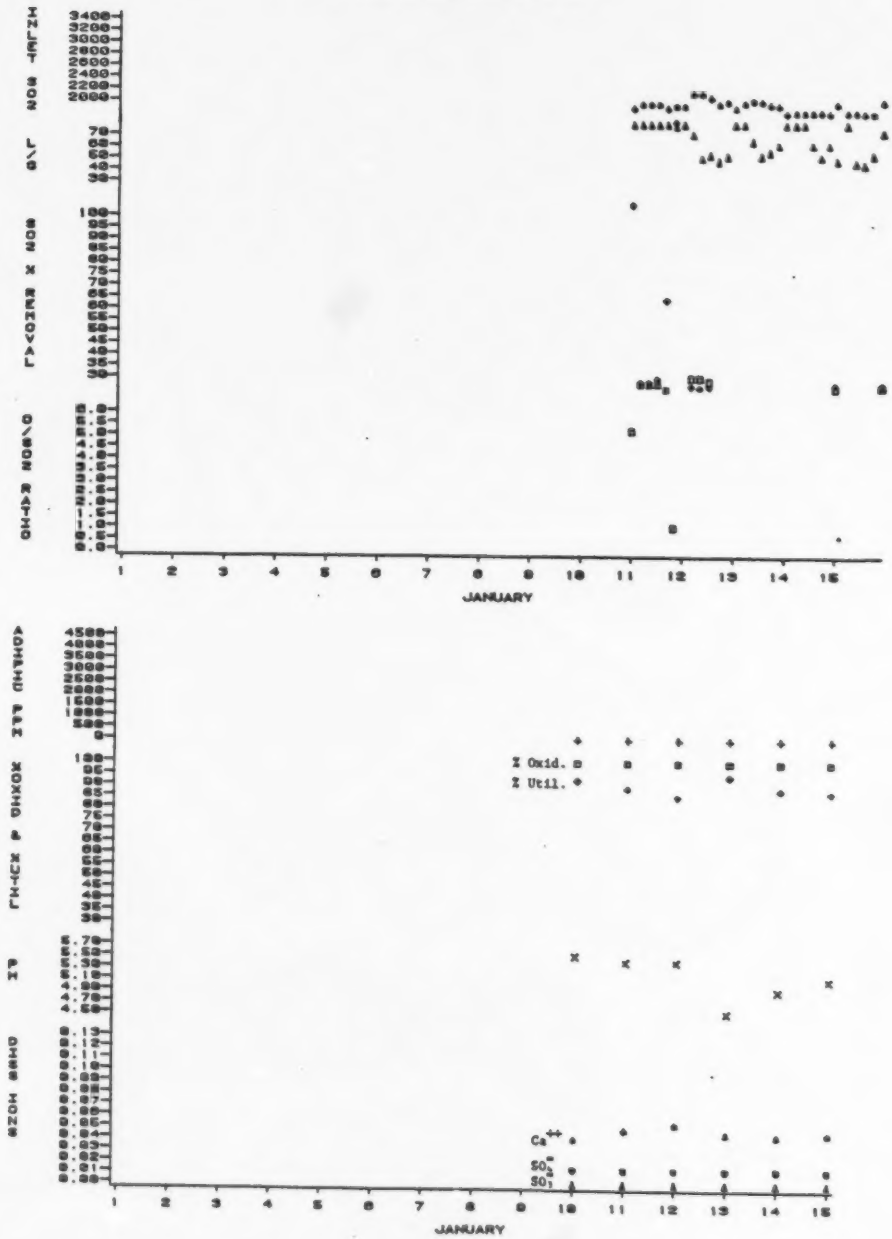
Module S-1 (Tray Tower) - Natural Oxidation (Adipic Acid)

SCRUBBER MODULE S-1



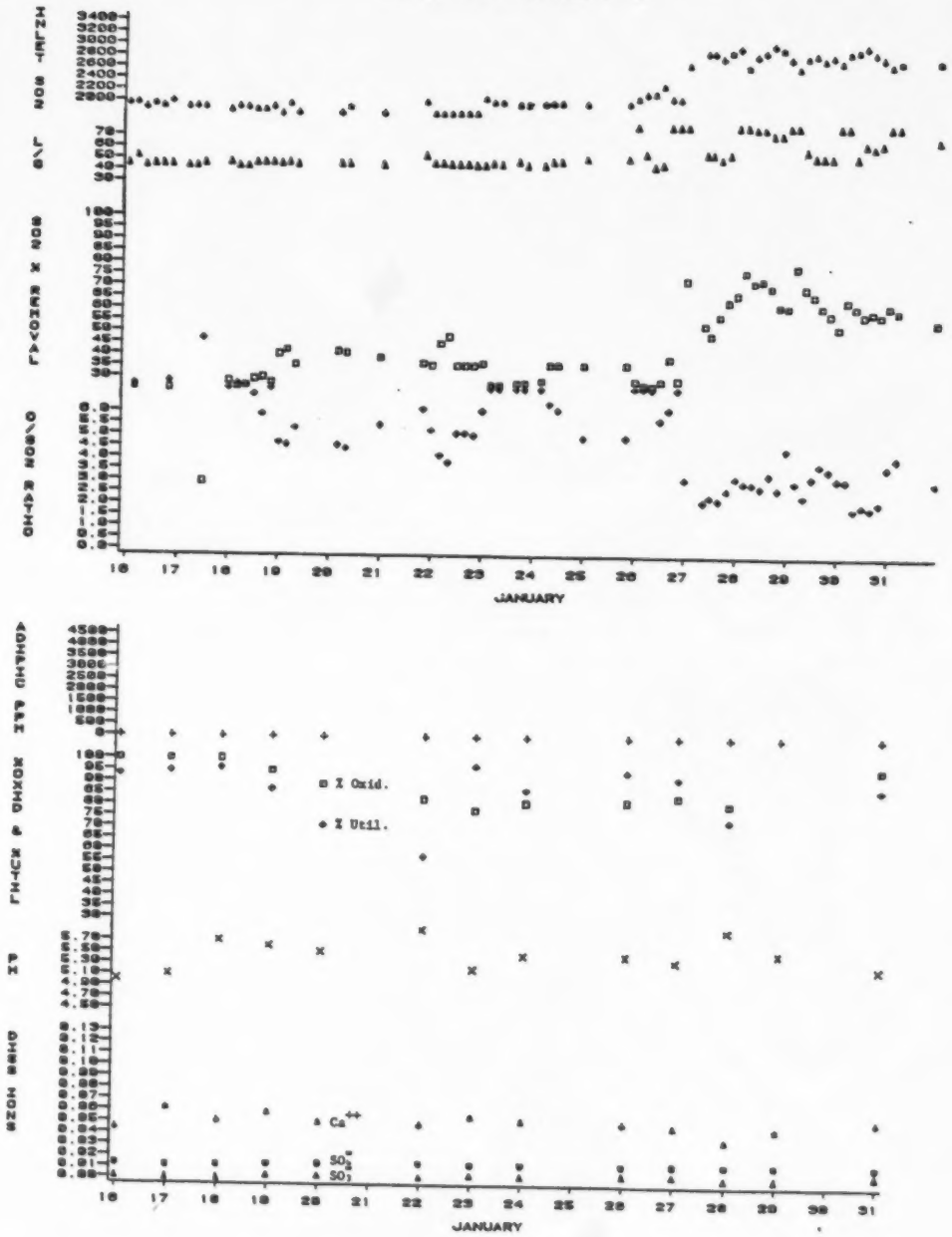
Module S-1 (Tray Tower) - Natural Oxidation (Adipic Acid)

SCRUBBER MODULE S-2



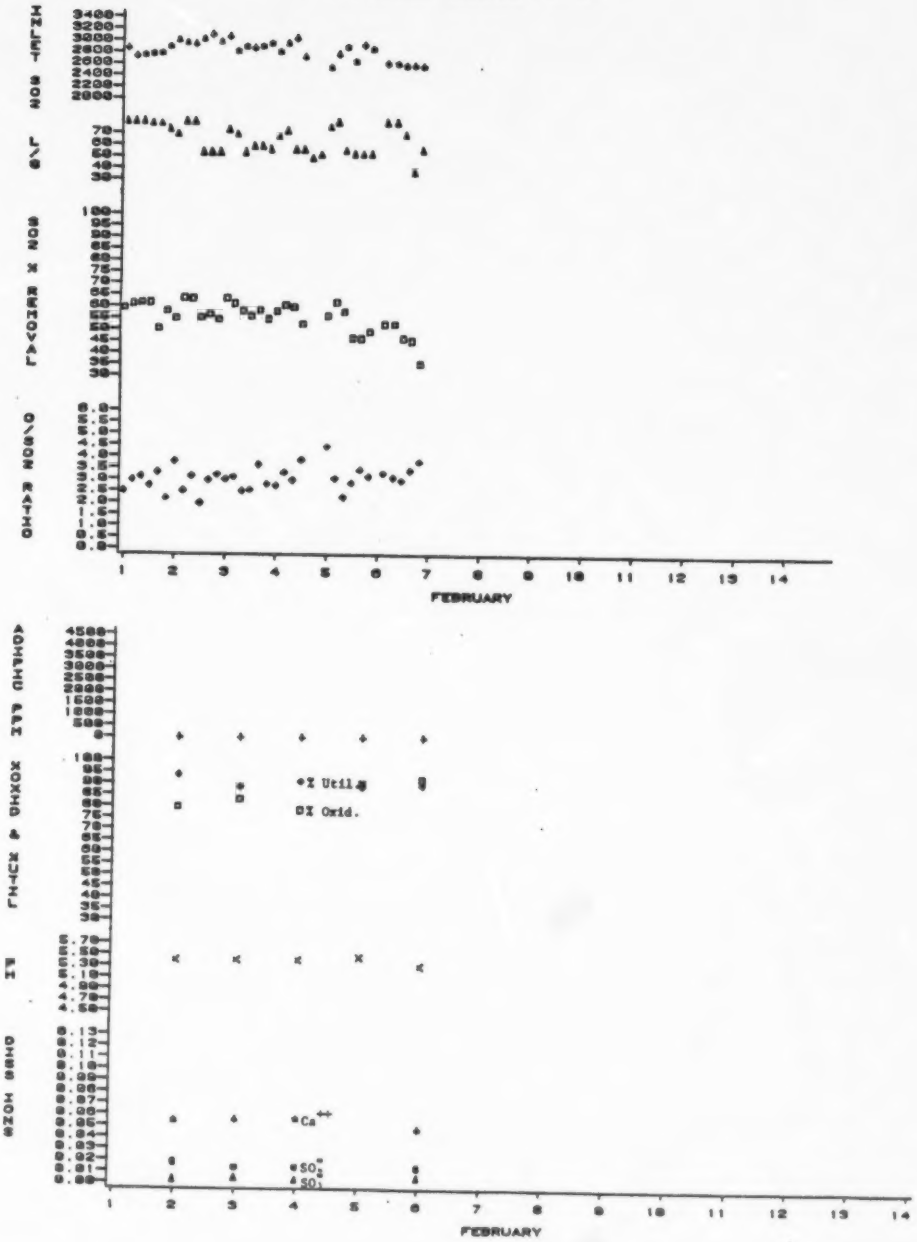
Module S-2 - Forced Oxidation (Baseline)

SCRUBBER MODULE S-2



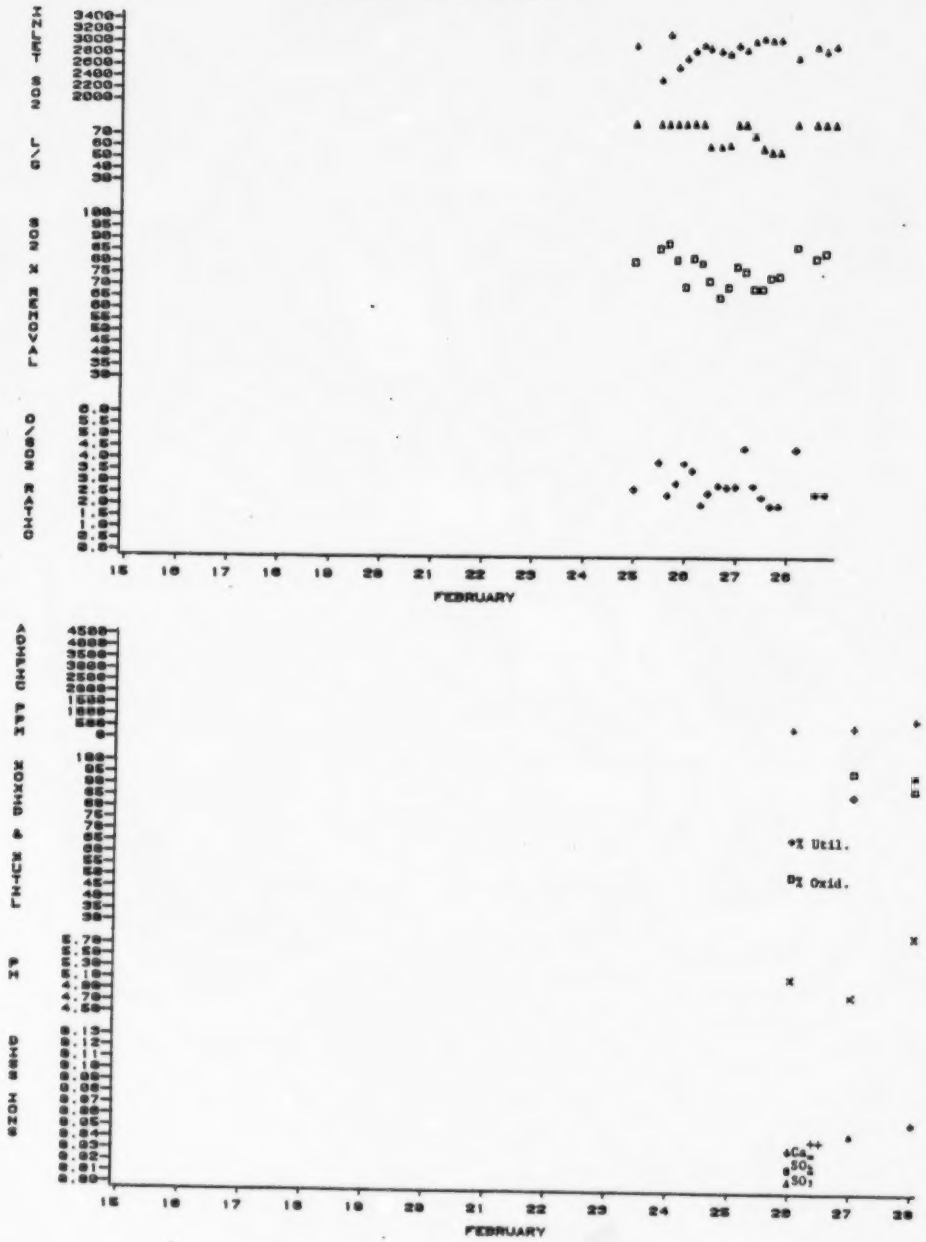
Module S-2 - Forced Oxidation (Baseline)

SCRUBBER MODULE S-2



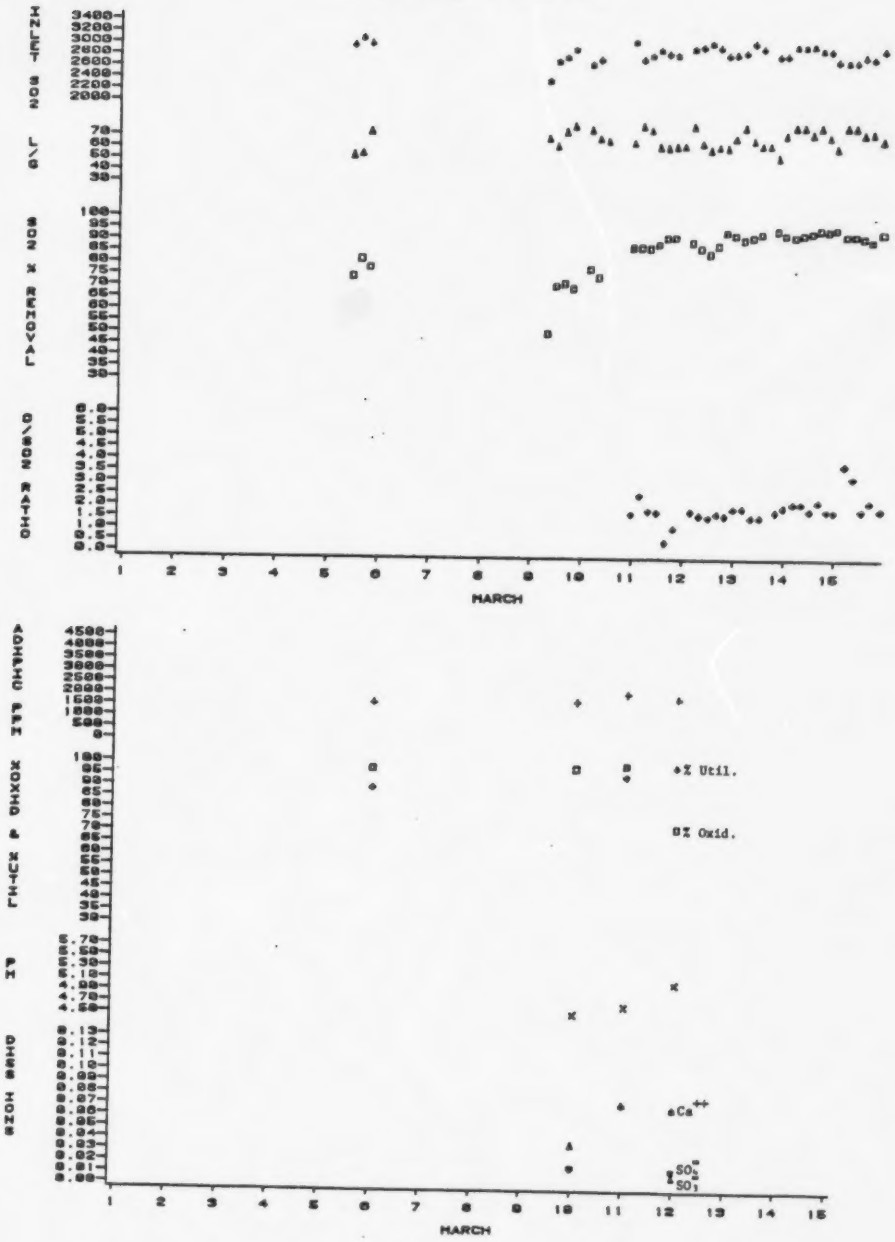
Module S-2 - Forced Oxidation (Baseline)

SCRUBBER MODULE S-2



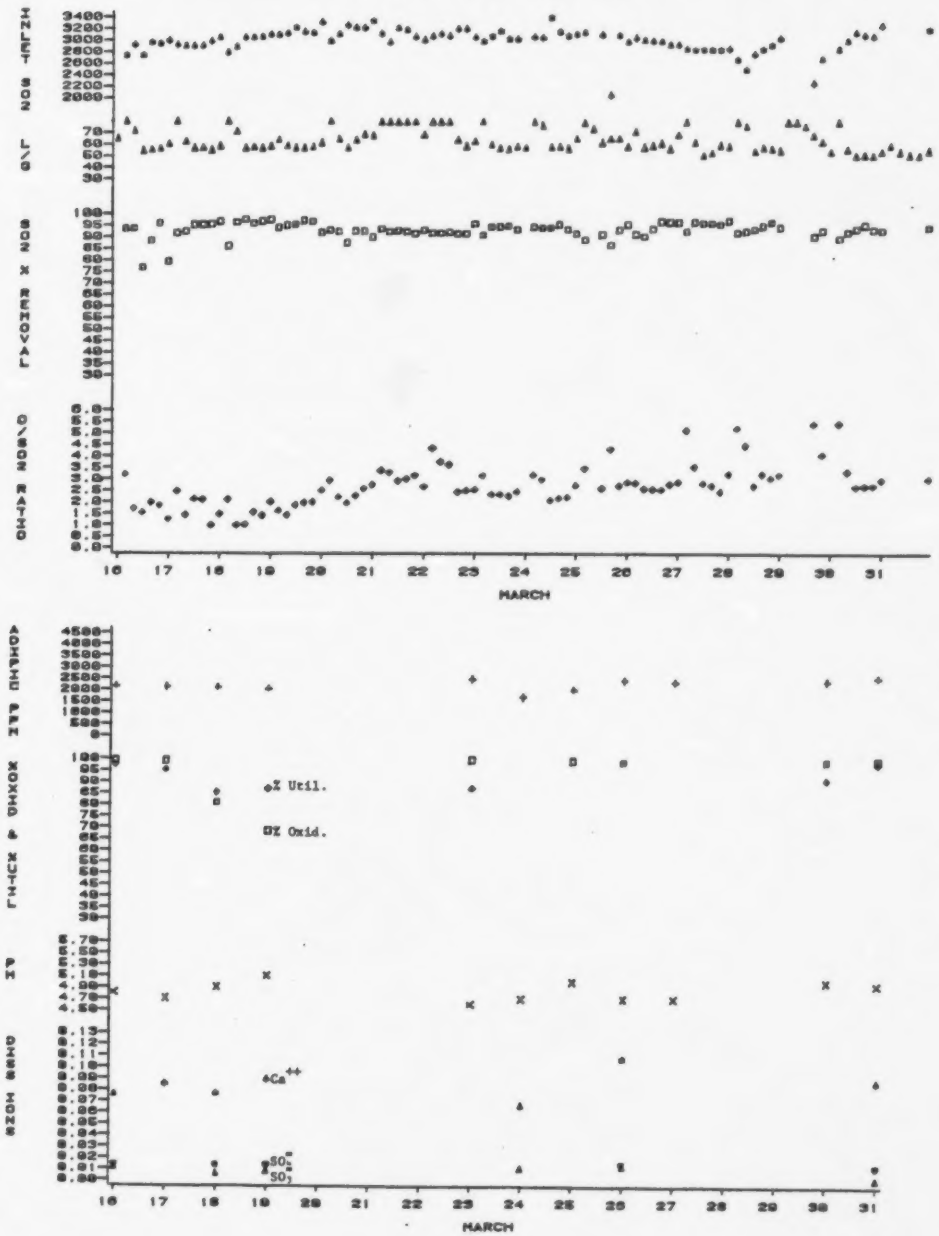
Module S-2 - Forced Oxidation (Adipic Acid)

SCRUBBER MODULE S-2



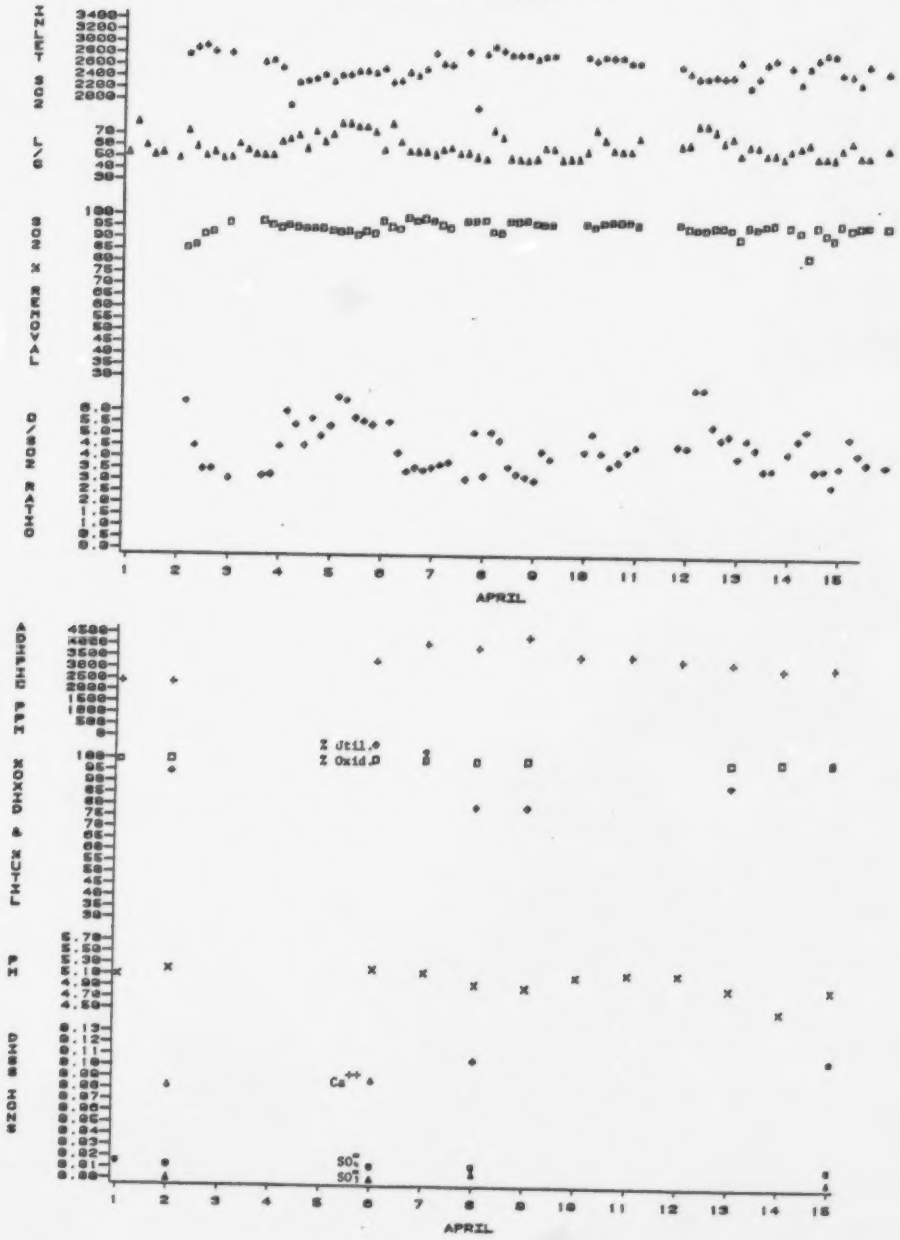
Module S-2 - Forced Oxidation (Adipic Acid)

SCRUBBER MODULE S-2



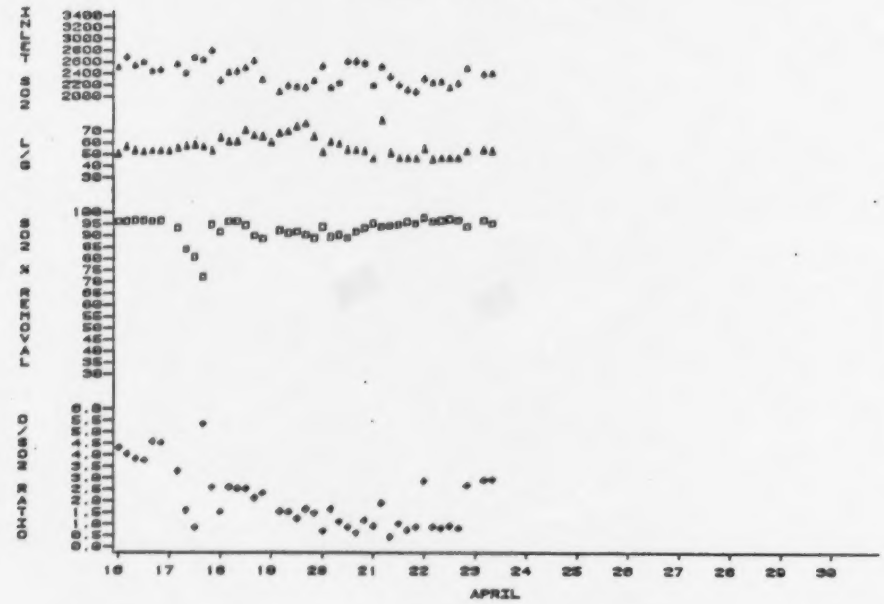
Module S-2 - Forced Oxidation (Adipic Acid)

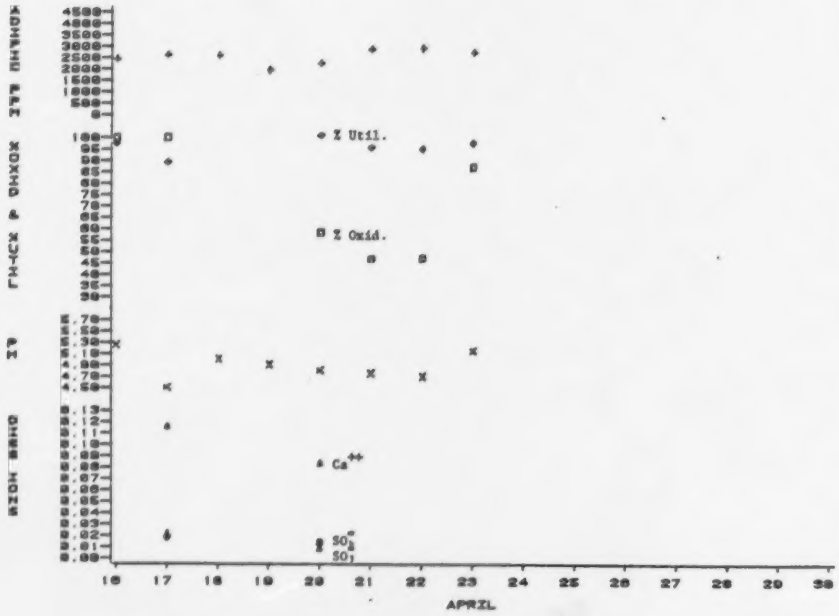
SCRUBBER MODULE S-2



Module S-2 - Forced Oxidation (Adipic Acid)

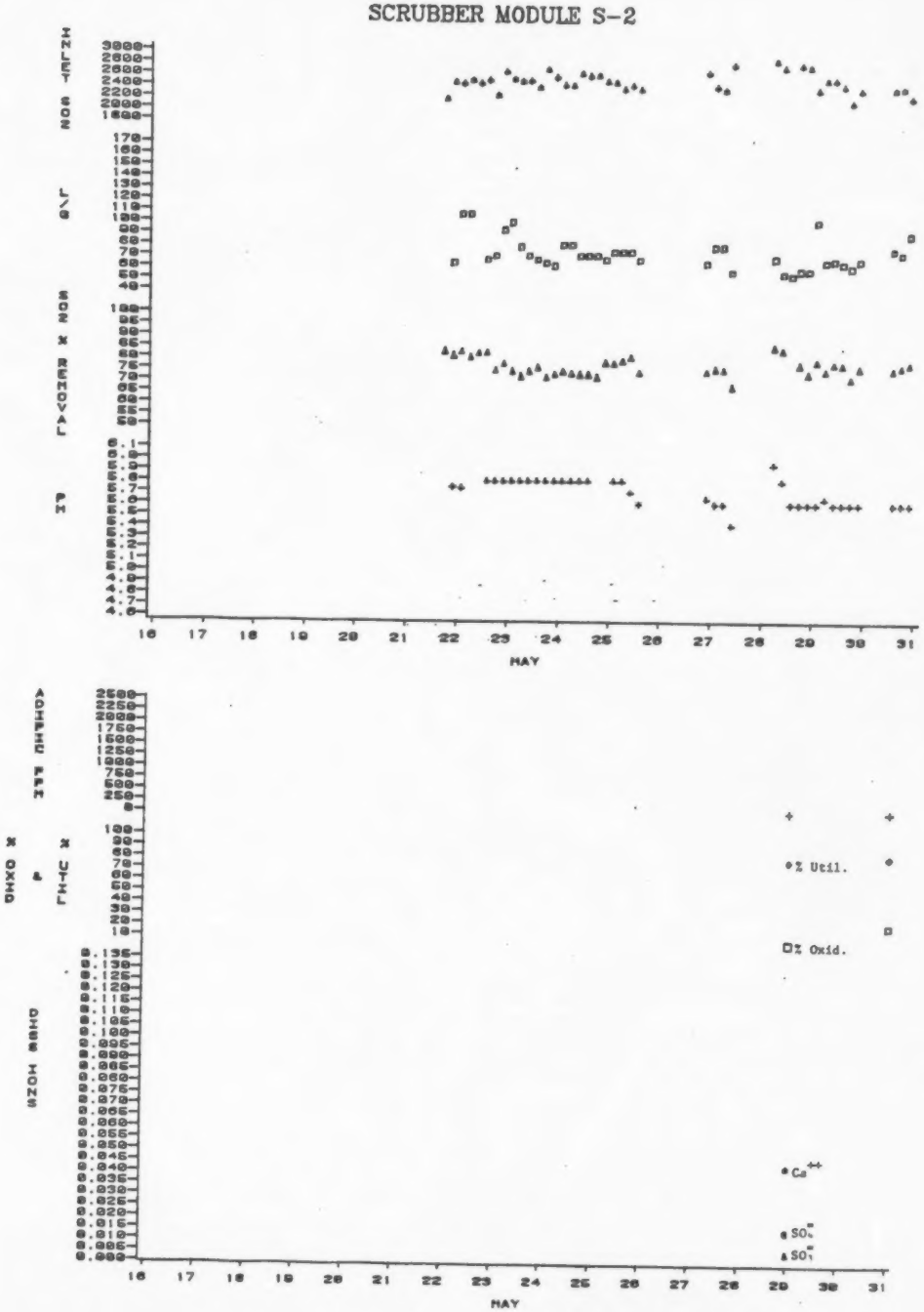
SCRUBBER MODULE S-2





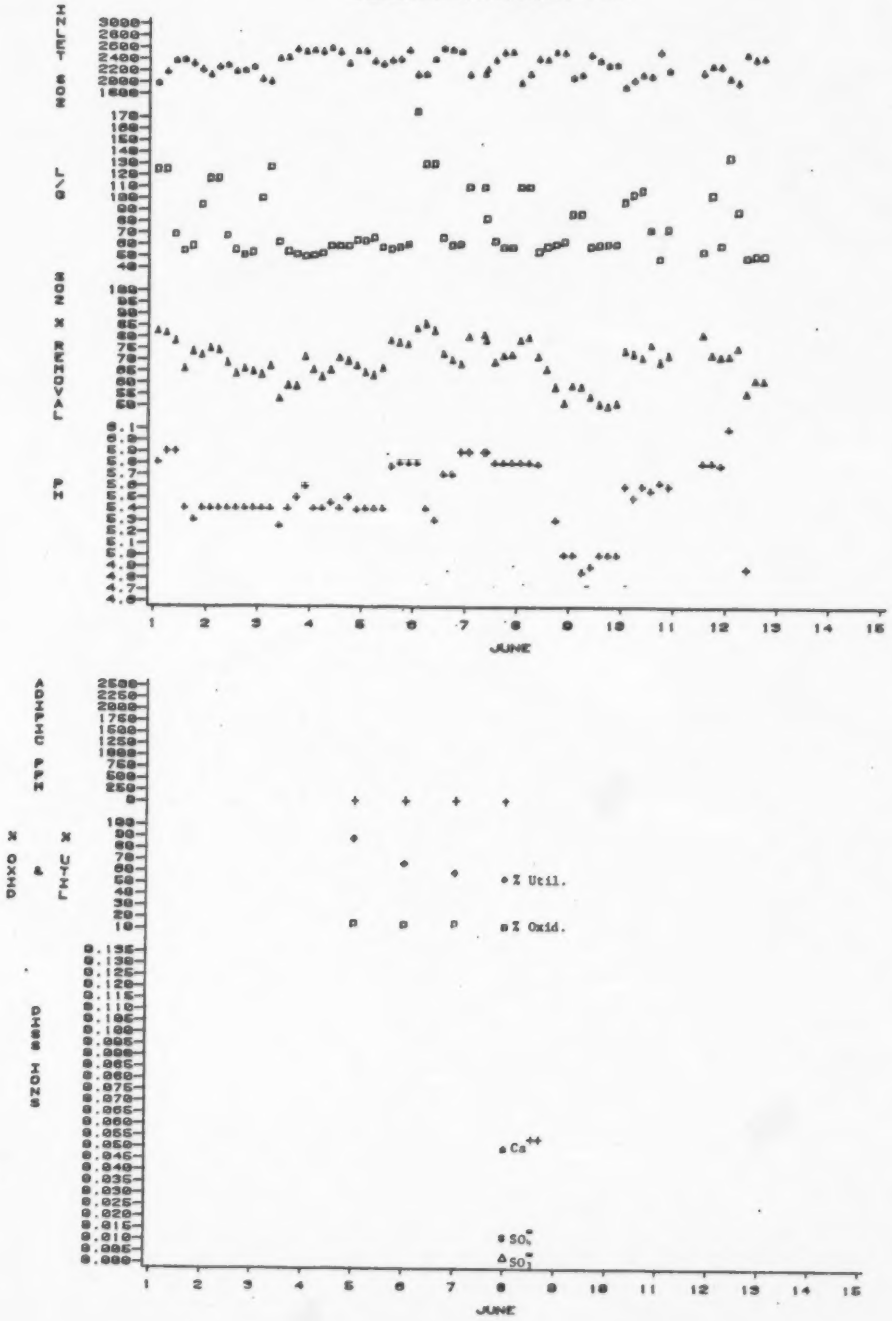
Module S-2 - Forced Oxidation (Adipic Acid)

SCRUBBER MODULE S-2



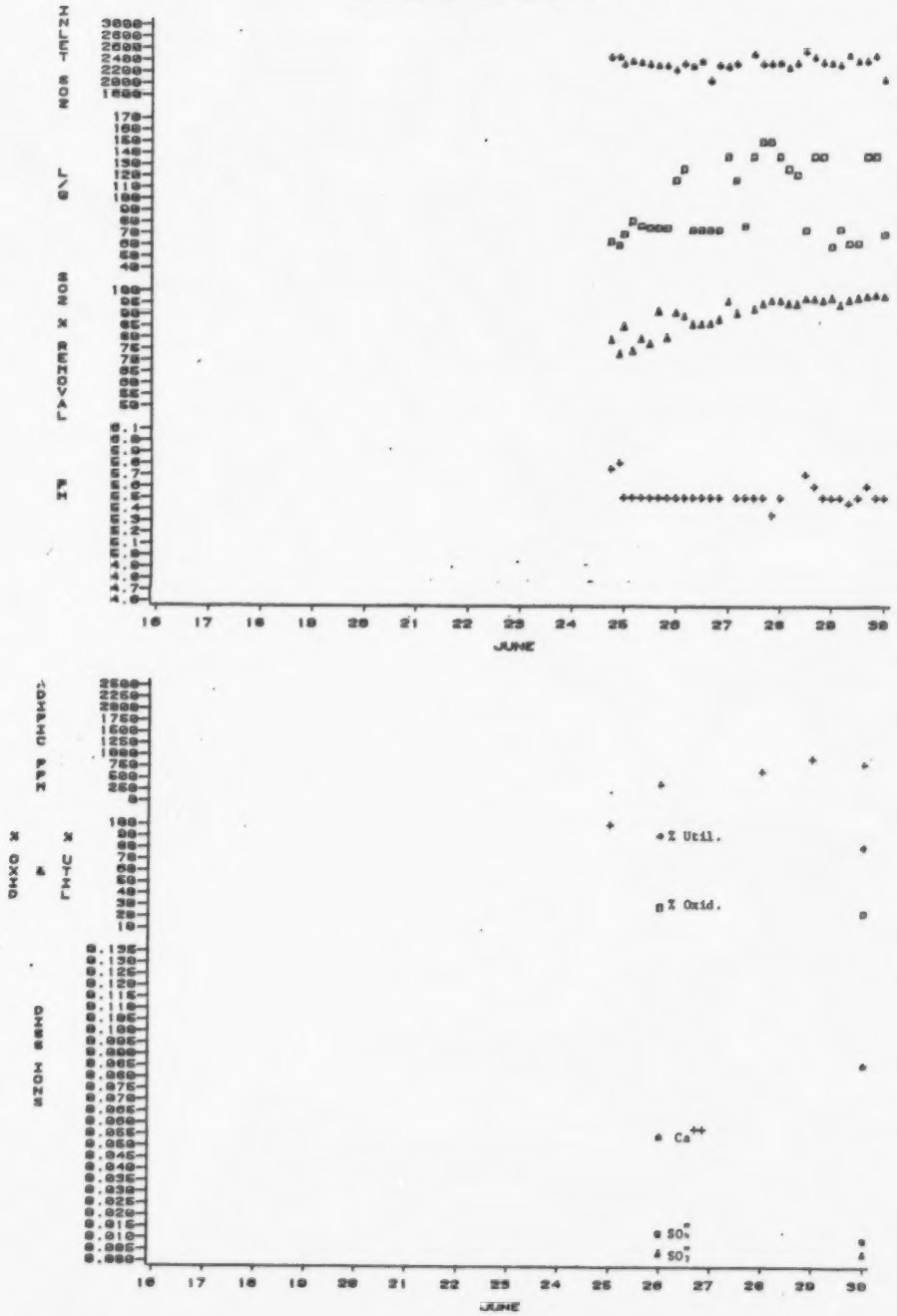
Module S-2 - Natural Oxidation (Baseline)

SCRUBBER MODULE S-2



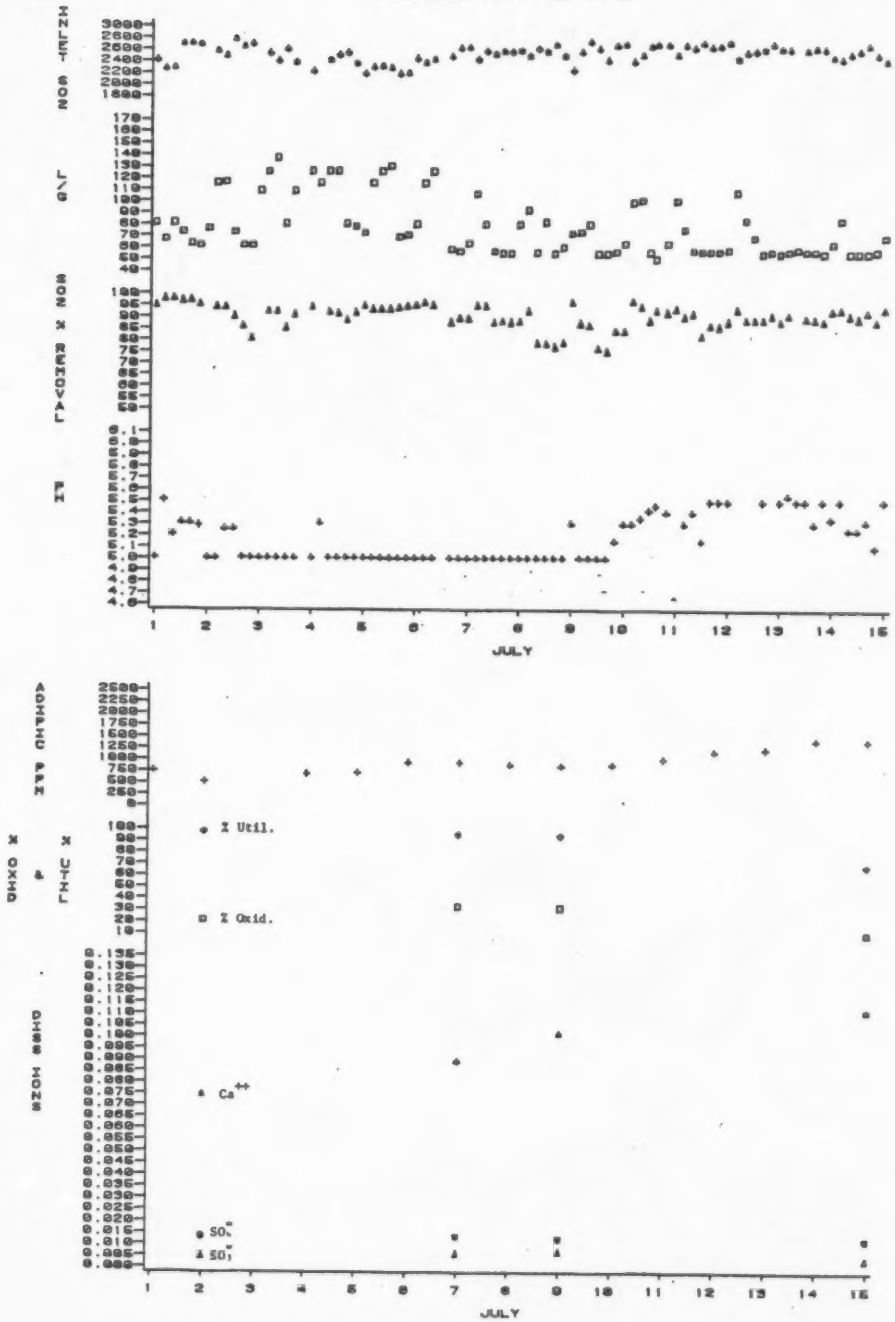
Module S-2 - Natural Oxidation (Baseline)

SCRUBBER MODULE S-2



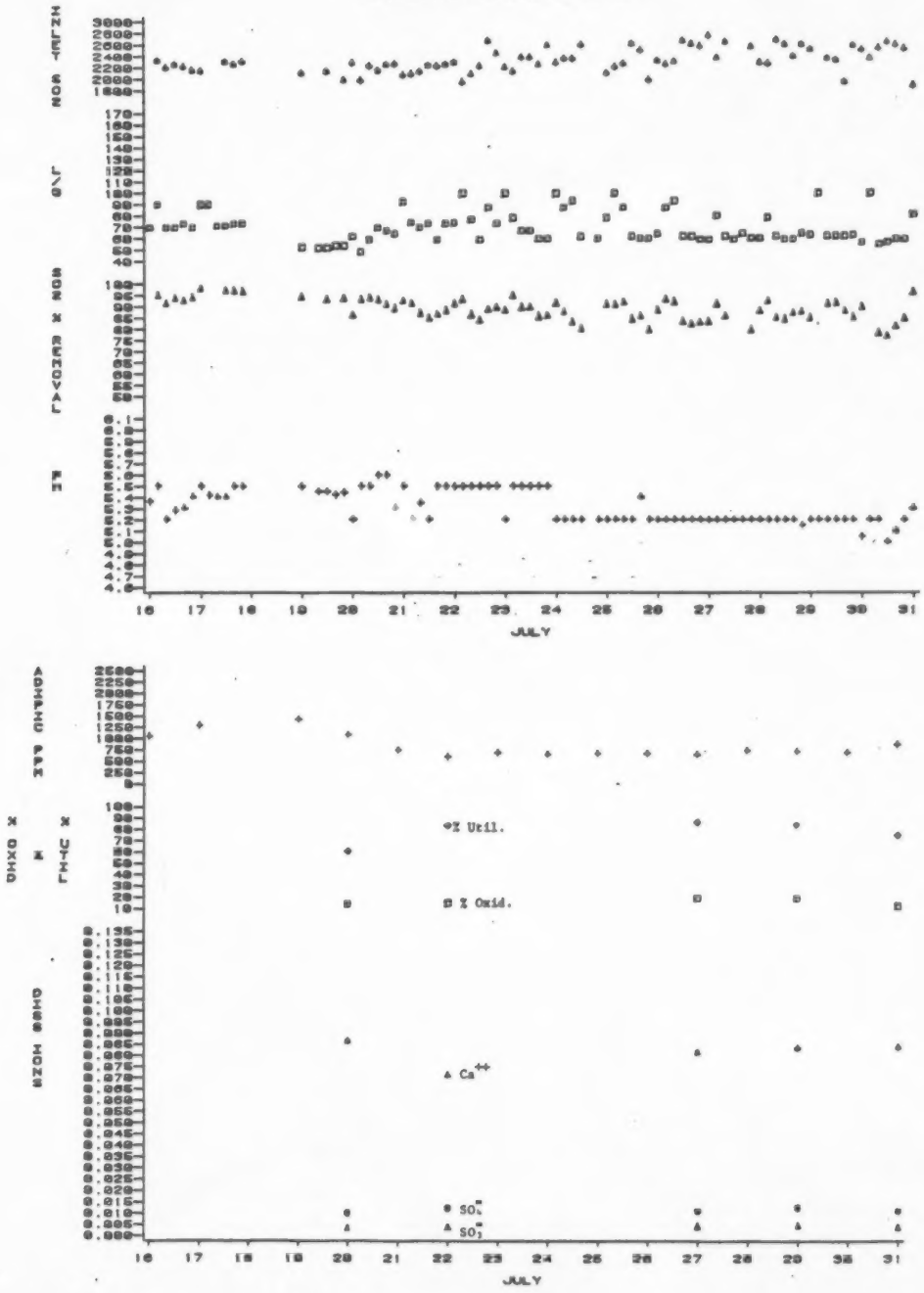
Module S-2 - Natural Oxidation (Adipic Acid)

SCRUBBER MODULE S-2



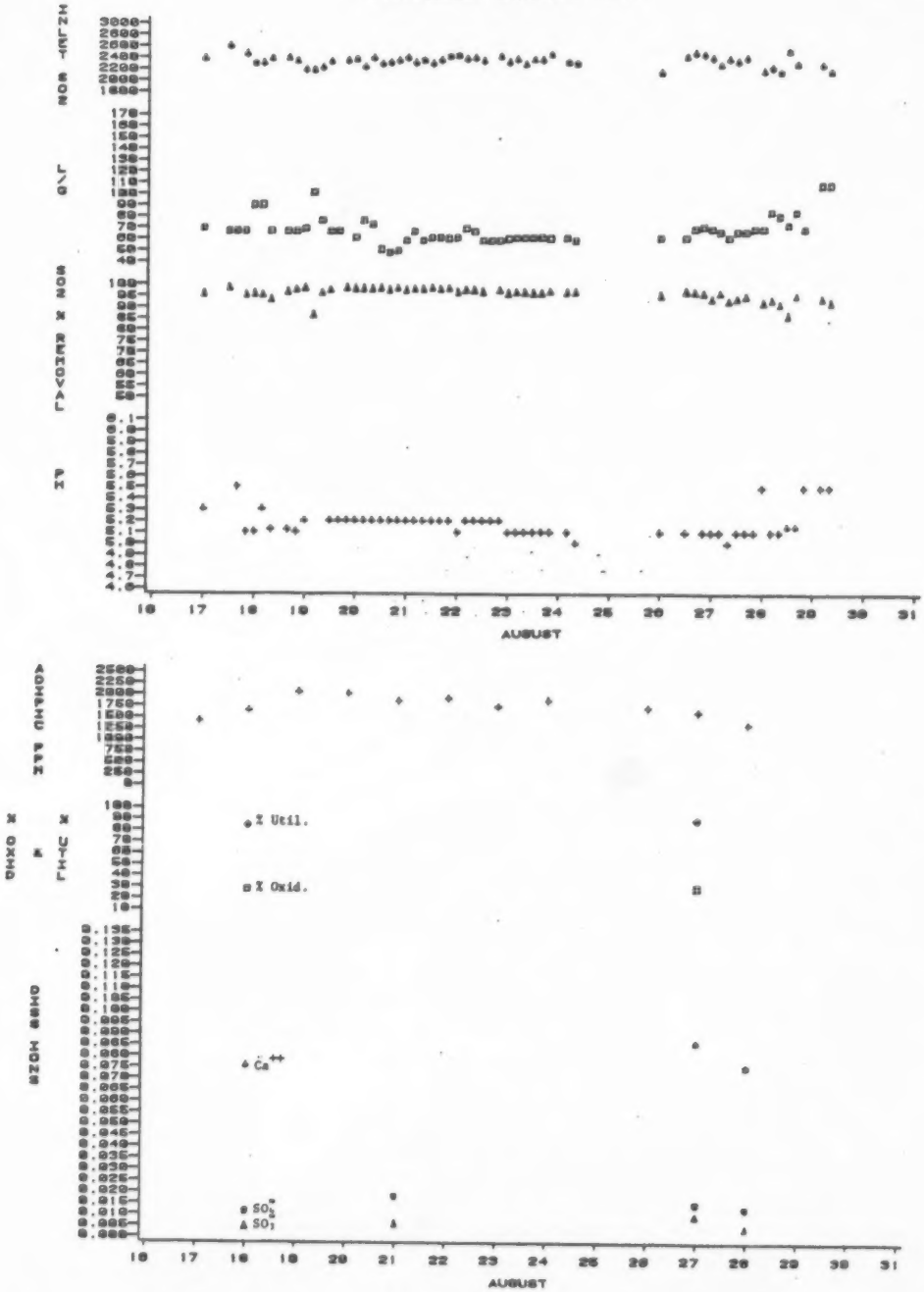
Module S-2 - Natural Oxidation (Adipic Acid)

SCRUBBER MODULE S-2



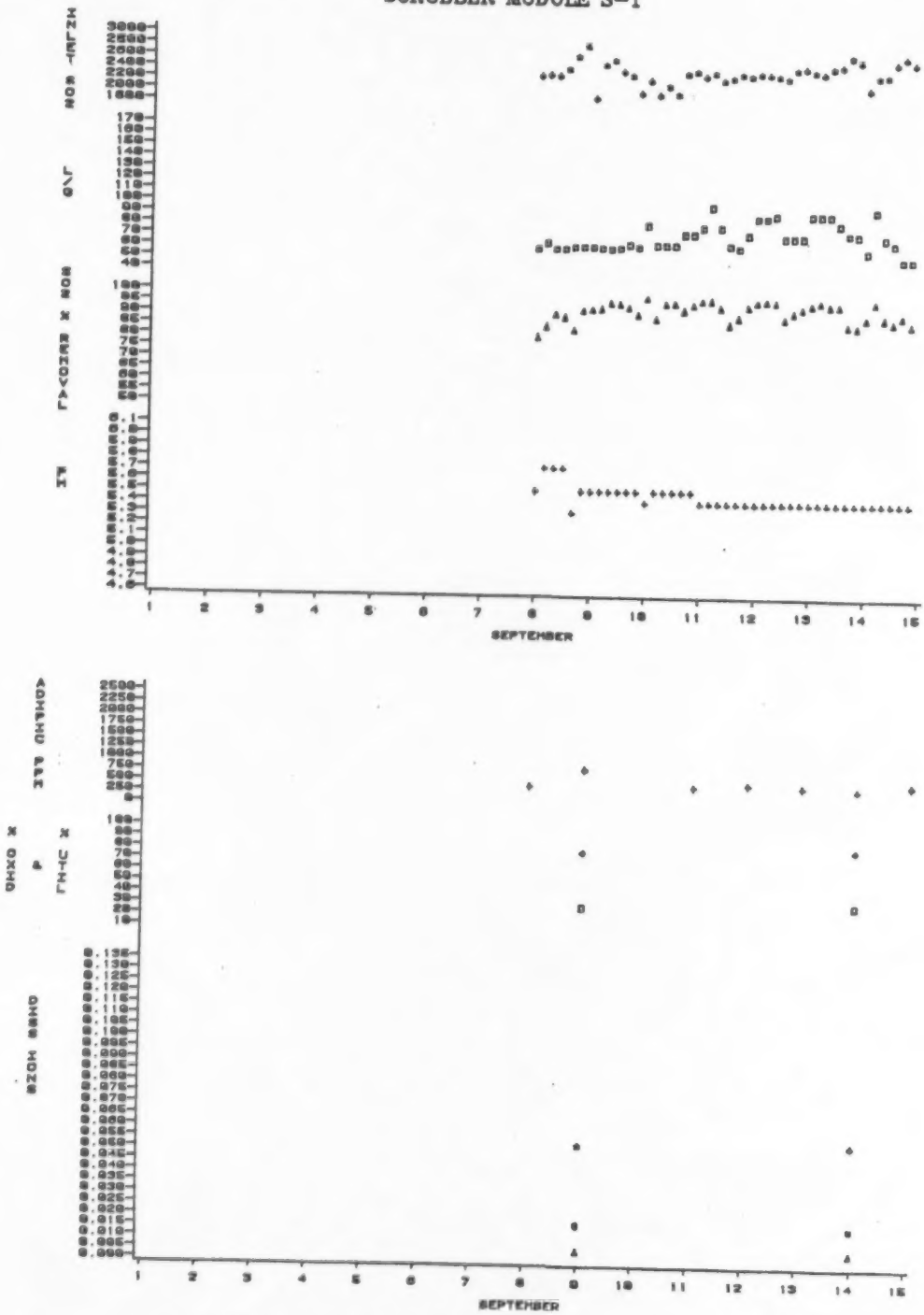
Module S-2 - Natural Oxidation (Adipic Acid)

SCRUBBER MODULE S-2



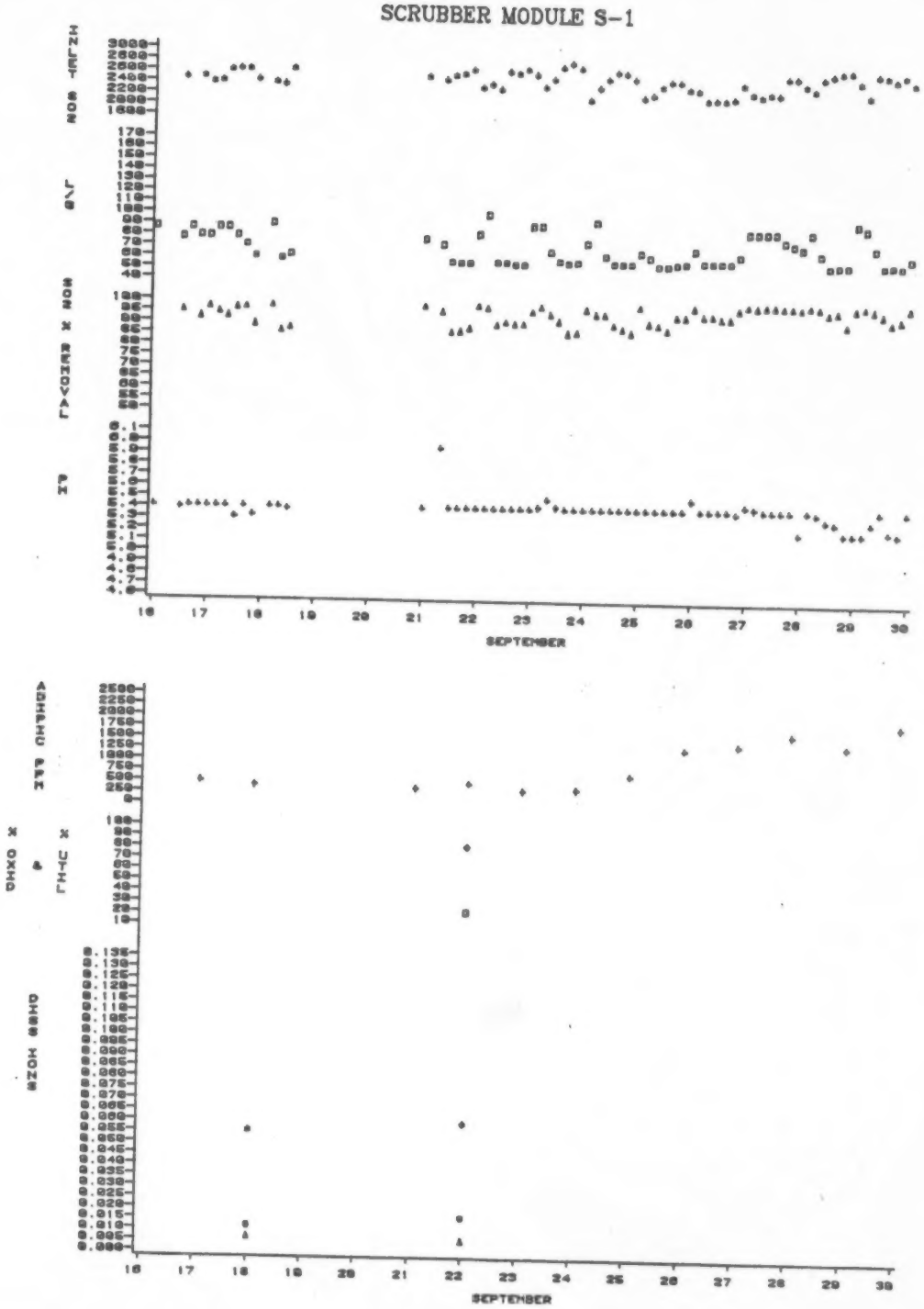
Module S-2 - Natural Oxidation (Adipic Acid)

SCRUBBER MODULE S-1



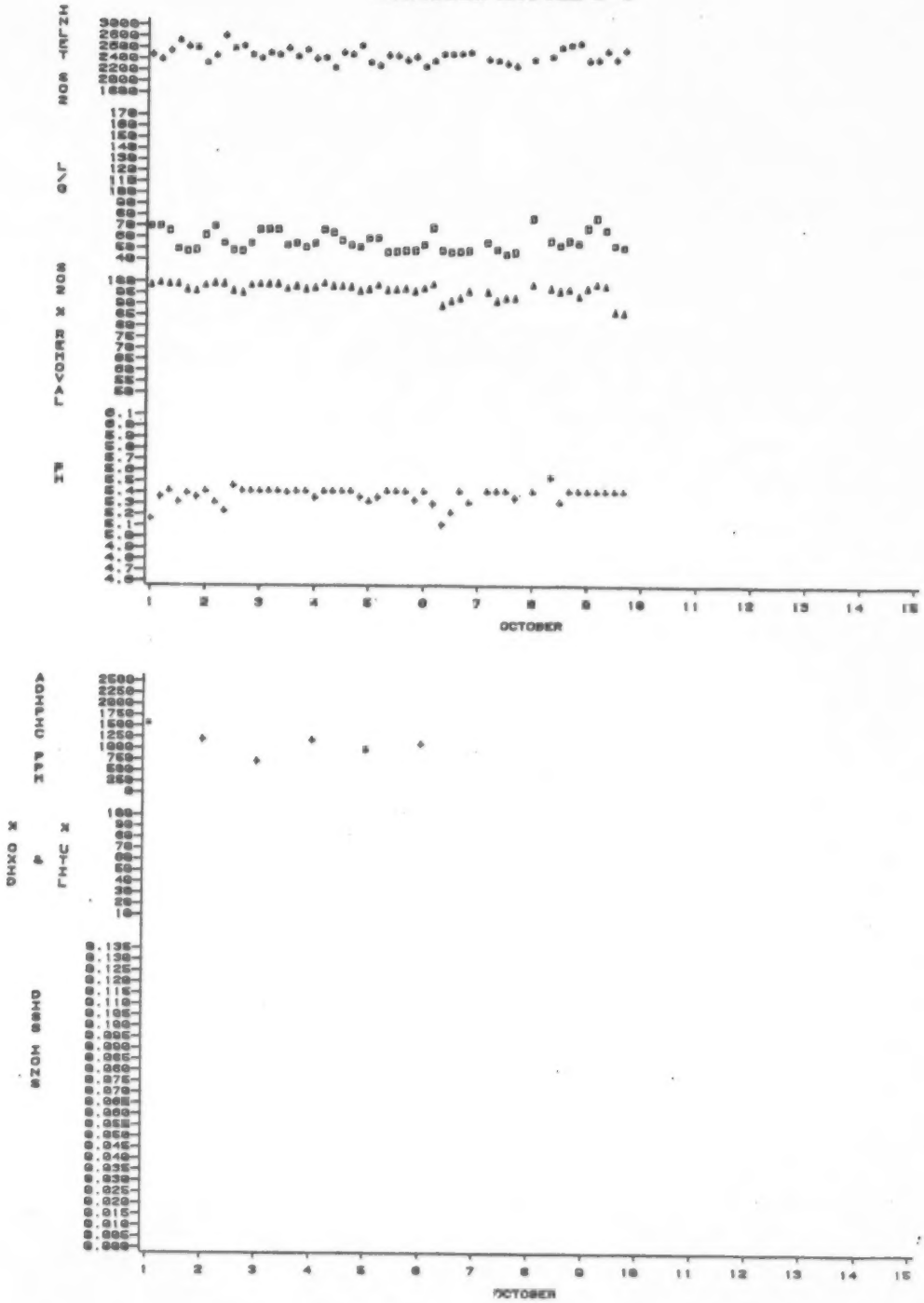
Module S-1 (Tray Tower) - Natural Oxidation (DBA)

SCRUBBER MODULE S-1



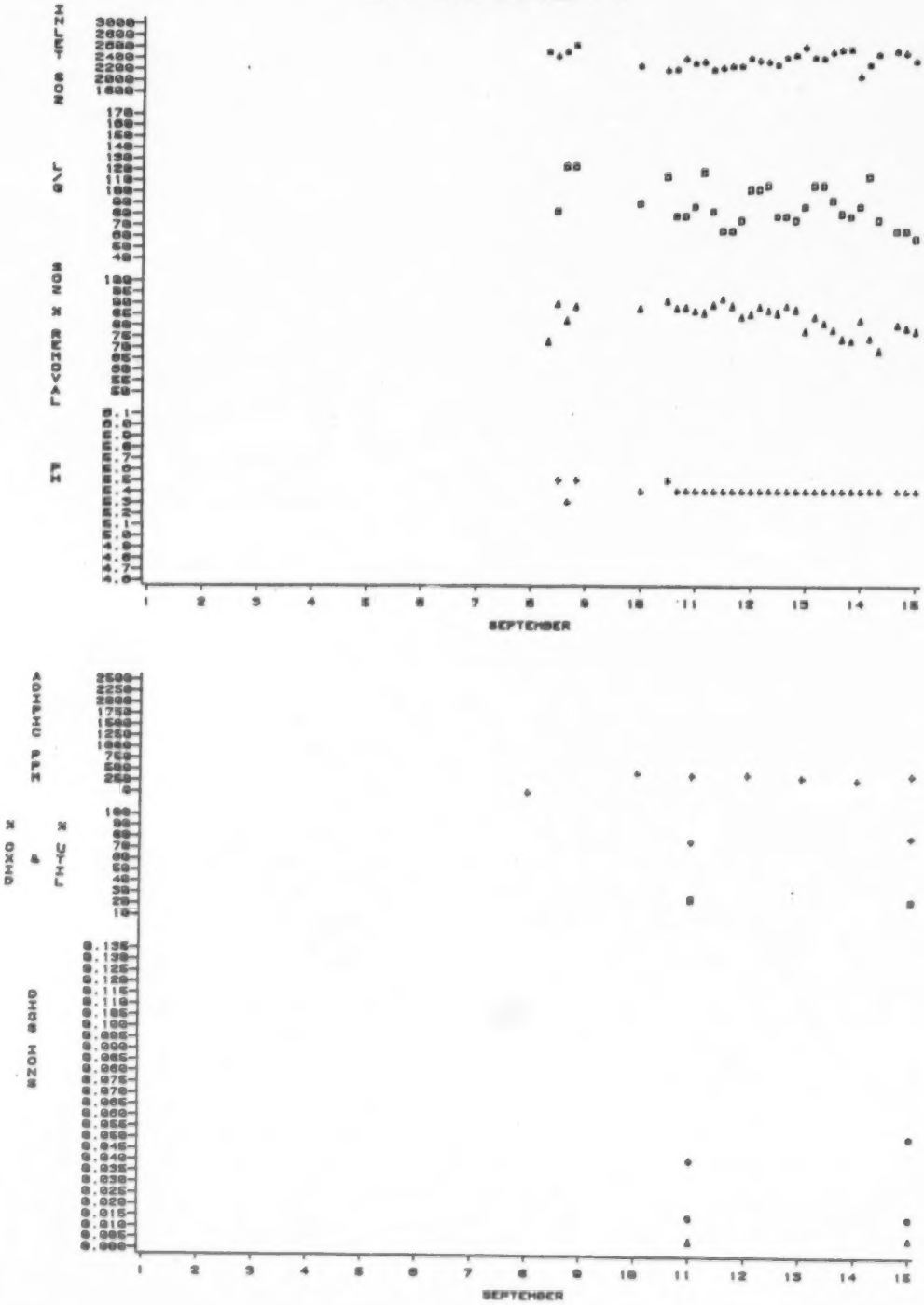
Module S-1 (Tray Tower) - Natural Oxidation (DBA)

SCRUBBER MODULE S-1



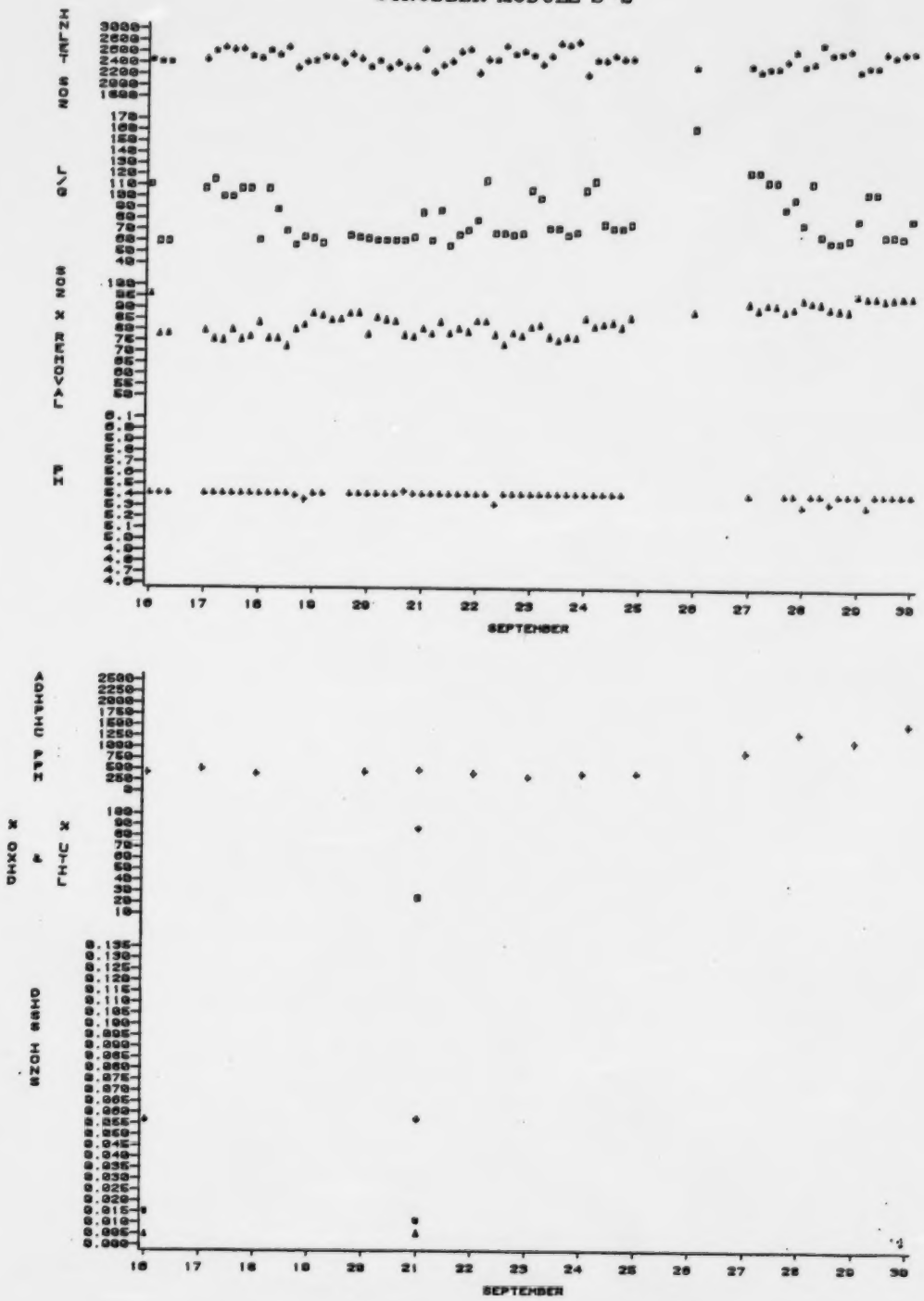
Module S-1 (Tray Tower) - Natural Oxidation (DBA)

SCRUBBER MODULE S-2



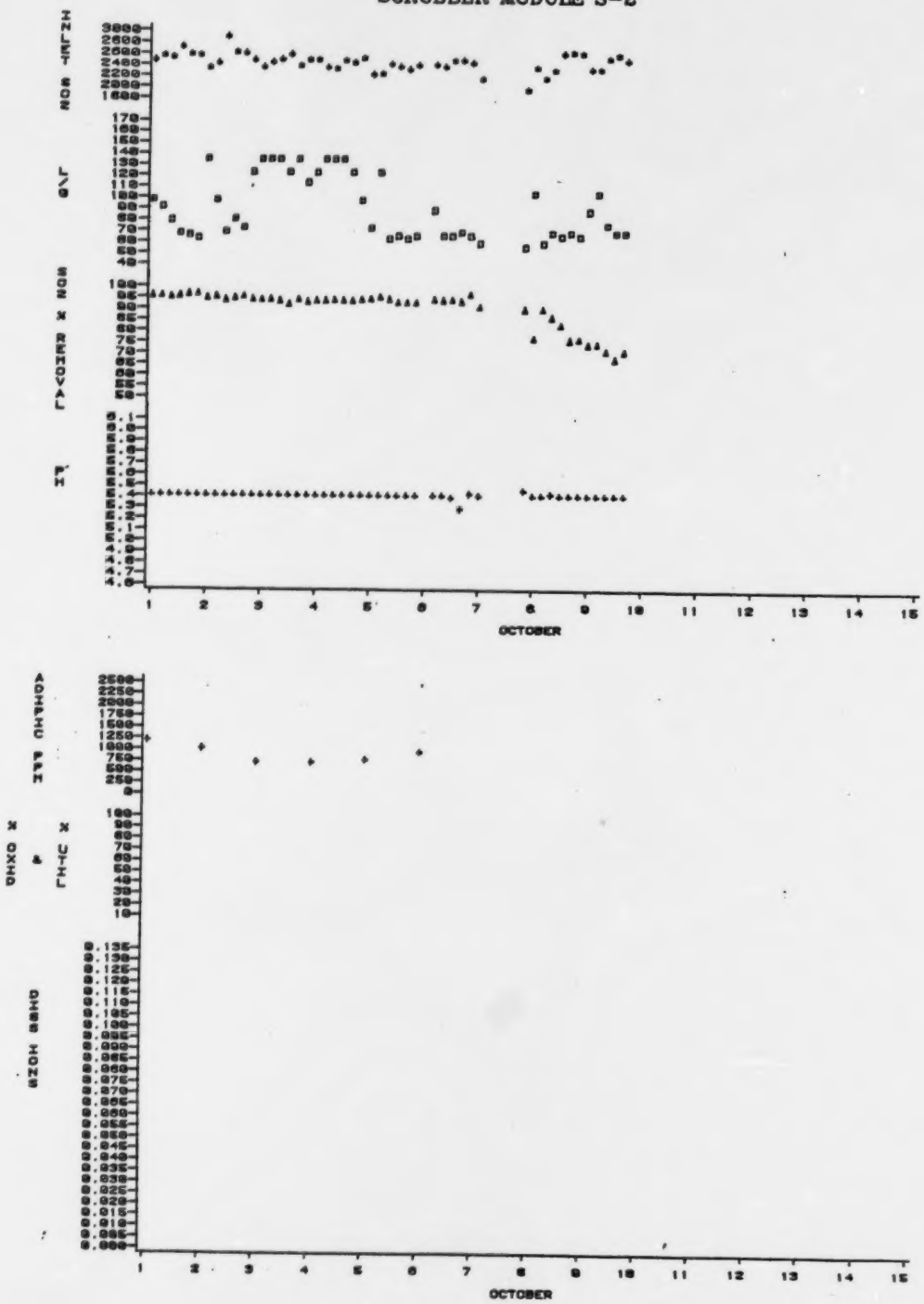
Module S-2 - Natural Oxidation (DBA)

SCRUBBER MODULE S-2



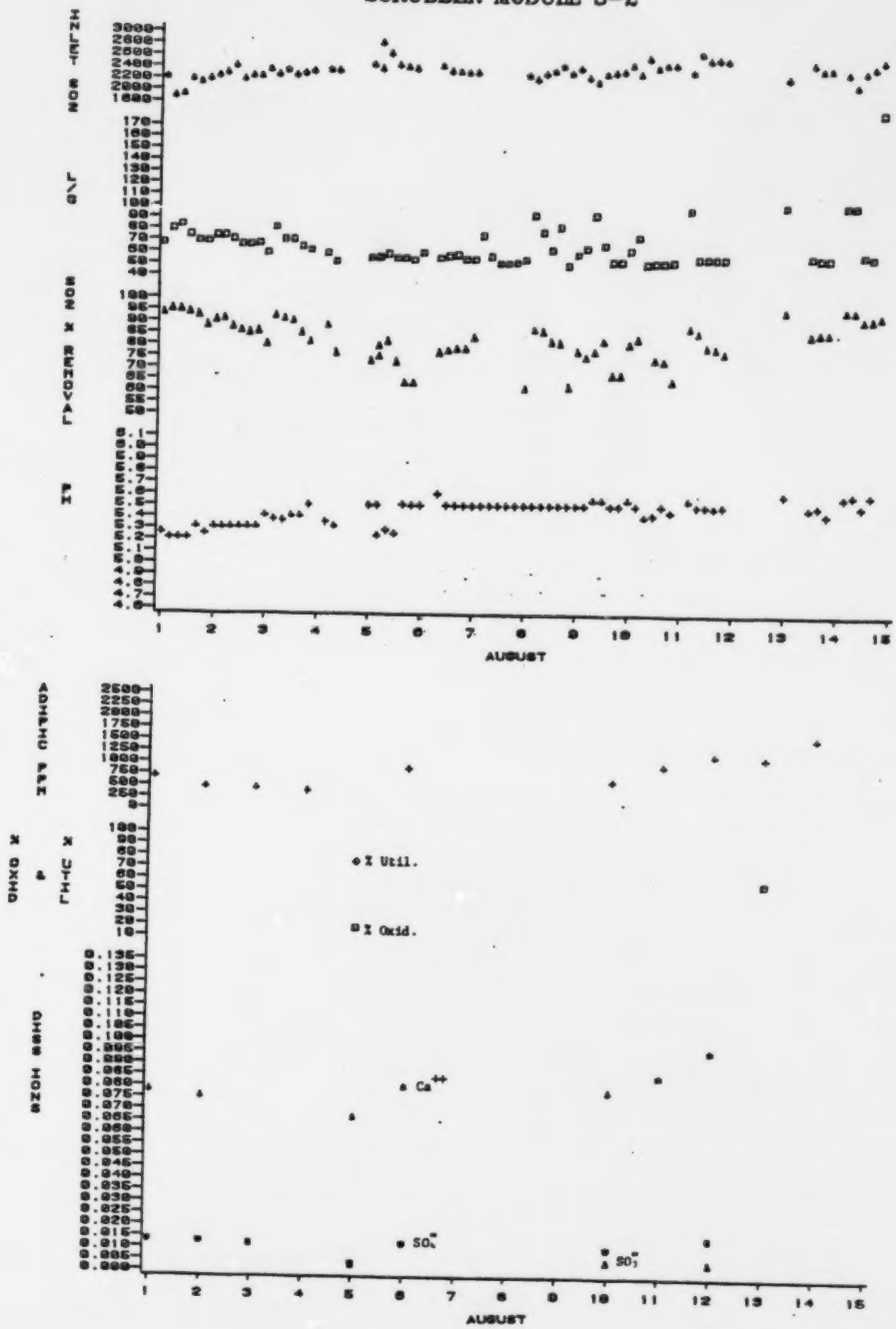
Module S-2 - Natural Oxidation (DBA)

SCRUBBER MODULE S-2



Module S-2 - Natural Oxidation (DBA)

SCRUBBER MODULE S-2



Module S-2 - Natural Oxidation (Adipic Acid)

APPENDIX D

COST ANALYSIS OF OPTIONS TO UPGRADE C.U.'s SOUTHWEST UNIT NO. 1 SCRUBBING SYSTEM

SECTION 1

SUMMARY AND DISCUSSION

1.1 STUDY BASIS

A number of alternatives have been considered to improve SO_2 removal efficiency (meet 1.2 lb SO_2/MM Btu - 82 to 85 percent SO_2 removal) at Springfield City Utilities' Southwest Power Plant Unit No. 1. This brief technical note presents a cost comparison of four options:

Option 1 - Increased L/G in existing tray towers (Module S-2 is to be converted from TCA this fall)

Option 2 - Adipic Acid Addition

Option 3 - Dibasic Acid (DBA) Addition

Option 4 - Conversion of the absorbers to spray towers with an increase in L/G

Limestone classifiers are scheduled for installation next spring. This should improve the throughput of the limestone ball mills (thus providing a spare mill as planned in the original design). According to pilot and prototype test results, the smaller limestone grind should improve the SO_2 removal which should reduce the increase in L/G or additive feed rate required to reach ∿85 percent removal. Options 1, 2, 3, and 4 are evaluated at L/Gs and additive rates which do not include any technical benefit from the installation of the classifiers. Options 1A, 2A, and 3A include lower L/Gs or additive feed rates (than in Options 1, 2, and 3) due to the presence of classifiers.

The method of cost analysis used was a present worth analysis. All project expenditures (capital and operating) are discounted back to year one using a

discount factor equal to the general inflation rate. Capital costs were expended in the first year (1982) for the additive options (2, 3, 2A, and 3A) while capital for increased L/G or spray towers (Options 1, 1A, and 4) were assumed to be spent in both the first and second years. The general inflation rate and corresponding O&M escalation rates consistent with C.U.'s long-term planning basis were assumed for this study and are defined in Section 2.

1.2 RESULTS

Figures 1-1 (no credit for classifiers) and 1-2 (credit for classifiers) summarize the results. In both cases, the DBA option is the most attractive option through the 15 year period (1982-1996). The tray tower with increased L/G becomes cheaper than the adipic acid option after 6 years if no credit for the limestone classifiers is assumed. This crossover point is 9 years if credit for the classifiers is estimated. The conversion to a spray tower is expensive, and the conversion has a number of technical uncertainties at this time.

1.3 DISCUSSION OF UNCERTAINTIES

Obviously, both technical and economic uncertainties make this analysis somewhat difficult to interpret. High inflation rates and relatively low cost of money (assumed for municipal utility) penalize adipic acid relative to more capital intensive options. However, DBA and adipic acid both appear to be attractive options relative to the more technically uncertain ones. Factors influencing the selection of each option are presented in the following discussion.

Dibasic Acid

- The cost of DBA is based on a quote from DuPont for shipping an 80 percent solution to Springfield. Conversations with Monsanto indicate the delivered cost of 20% DBA solution could be substantially cheaper (30-40% cost reduction). This is being investigated further.

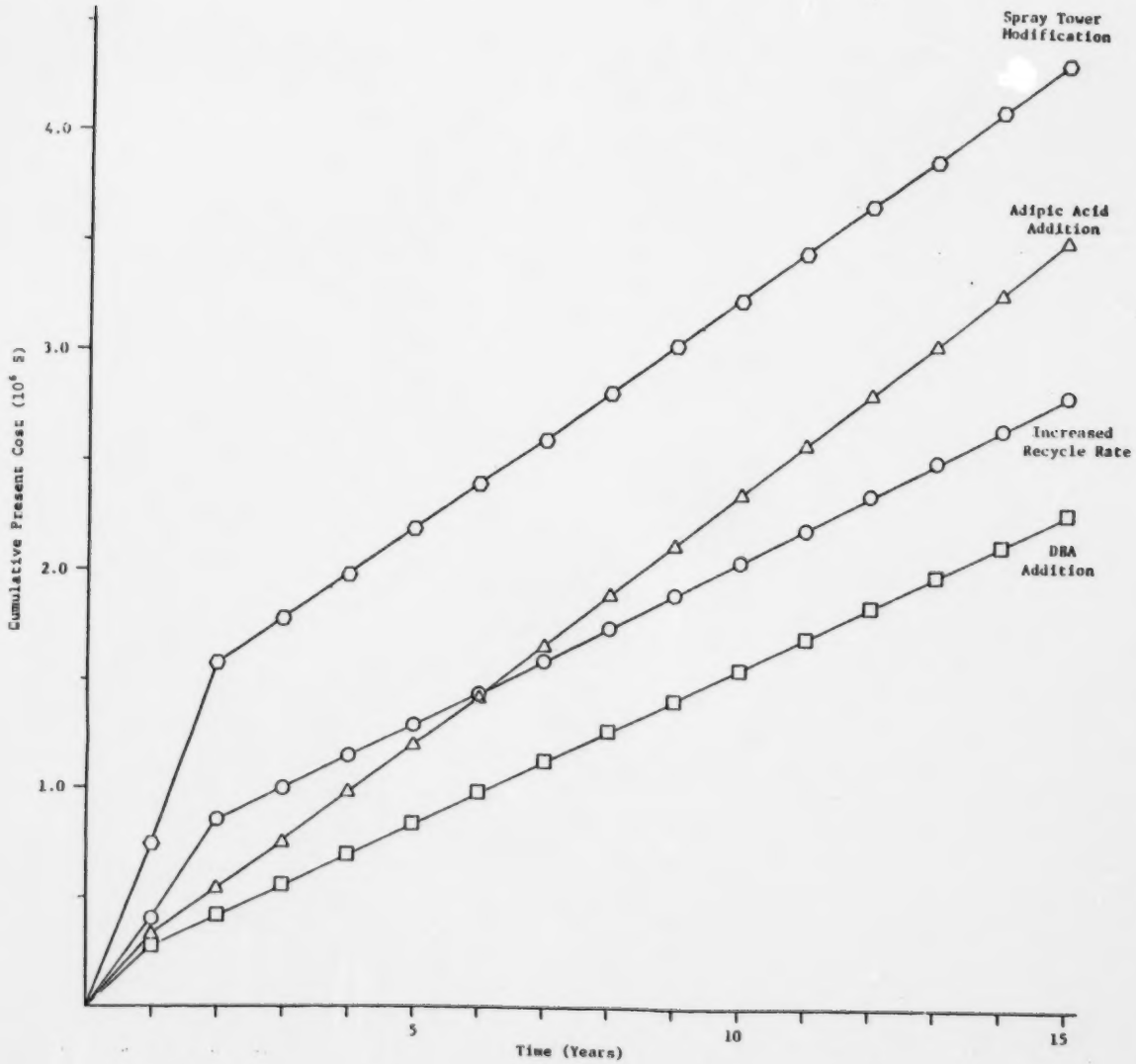


Figure D-1. Cumulative present cost for options 1, 2, 3, and 4.

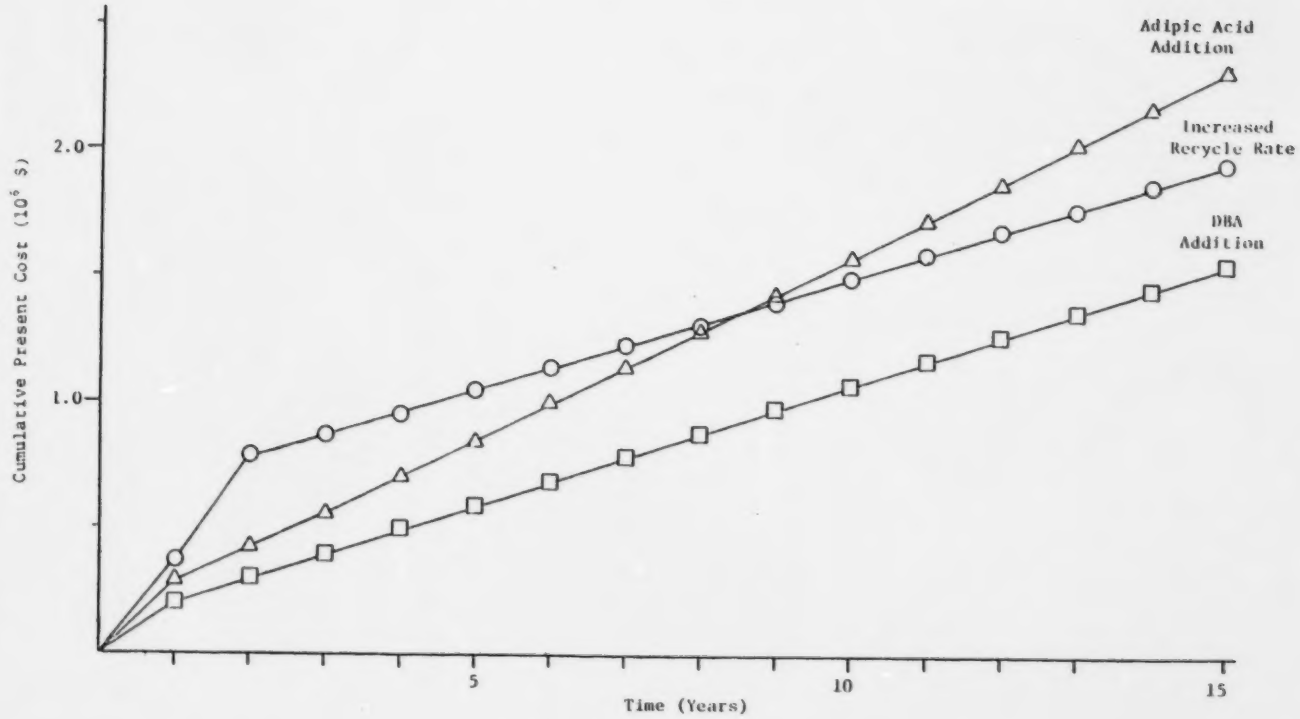


Figure D-2. Cumulative present cost for options 1A, 2A, and 3A.

- The DBA feed system should be more simple (and cheaper) than the adipic acid feed system since no solids handling is anticipated. However, a small immersion heater will be required. Since a full analysis of the control scheme has not yet been made, the DBA feed system was assumed to cost the same as the adipic acid feed system.

- Testing with DBA has not been completed at Springfield so no well-documented feed rate has been established. Based on pilot plant data, the DBA consumption should be about 20 percent higher than the adipic acid consumption rate. To break even with the tray tower/higher L/G option for 10 years (credit for classifiers) the DBA consumption could be above 30 percent higher than the adipic acid consumption.

- DBA seems to increase the sulfite oxidation based on preliminary analysis. This leads to improved filter cake properties, but does not solve all dewatering problems. Continued tracking of dewatering performance with DBA is being conducted.

Tray Tower/Higher L/G

- Increased SO_2 removal has been obtained at SWPP by operating a second pump and increasing the L/G for $\sim$2 hours. However, long-term performance has not been documented. At high loads, slurry carryover could be a problem. Also, the gas throughput could be limited at an L/G of 80, but this has not been documented. If throughput is limited, additional holes could be made in the trays or the fan's inlet damper could be modified if carryover is not a problem. Prior to committing to this option, operation with two pumps in service should be tested for a month or more to identify potential operating problems.

- Cost of electricity for this option contains only production costs. Since no capital component is included, this option does not penalize the higher L/G case for using capacity which could be used to supply customers.

Adipic Acid Addition

- The adipic acid data base is the most extensive, and this option is the most certain one.

- This option is most negatively affected in comparison to others by the assumption of relatively high inflation rates.

- When assumptions are made concerning the reduced increase in required adipic acid consumption or L/G due to addition of limestone classifiers, the adipic acid option has a lower cost than the tray tower/higher L/G option for 9 years. A fairly conservative estimate was made for adipic acid savings. If adipic savings were greater, the crossover point would occur later and the adipic acid option would become a clear cut choice.

- Adipic feed rate might be further optimized by stopping feed during low load periods and spiking when required at higher load periods.

- Operation at low pH is possible with adipic acid and should lead to less plugging or scaling on the trays or demisters due to higher limestone utilization. No credit (reduced cost) for reduced limestone consumption has been taken, however.

Spray Tower

- This option is least attractive from an economic and technical basis. High gas velocities with associated carryover problems make this choice somewhat questionable on a technical basis.

1.4 CONCLUSIONS

- DBA is the preferred option at this point. Additional investigation into the actual consumption rate, delivered costs, and control scheme will be made.

- Adipic acid is less expensive than higher L/G for ∿9 years if an assumption of credit for classifiers is made. This option is most technically certain and would be the choice on that basis.

- Further testing with two pumps should be performed prior to selecting the higher L/G option.

- The spray tower option is not attractive from a technical or economic standpoint.

SECTION 2

RESULTS

The cost methodology used here is a present worth analysis. Capital expenditures are assumed to be made during the first or during the first and second years. (First is assumed to be 1982). The operating and maintenance costs were escalated by the appropriate inflation rate and then the present worth (in the first year, 1982) was calculated using the following equation:

$$P.W. = \frac{S}{(1 + i)^n}$$

where S is the cost in any year n, and i is the discount rate which has been assumed to be equal to the general inflation rate in this study. This is because the cost of money to City Utilities is closely tied to the municipal bond market and traditionally municipal bonds have paid interest at rates fairly close to the general inflation rate.

2.1 INFLATION ASSUMPTIONS

Table 2-1 shows the general, fuel oil, and coal inflation values which City Utilities is presently using for long-term planning. In this evaluation, capital and maintenance expenses have been assumed to escalate at the general inflation rate.

The cost of electricity (C.O.E.) for this study is the cost of production to City Utilities (no capital component) which is currently about 2.5 cents per kilowatt hour. Of this total, coal costs are about 75 percent. Therefore, 75 percent of the C.O.E. has been escalated at the coal inflation rate and the remaining 25 percent of the C.O.E. has been escalated at the

general inflation rate. The escalation rates for the C.O.E. are shown in Table 2-2.

TABLE 2-1. CITY UTILITIES' ESTIMATED INFLATION RATES FOR PURPOSES OF LONG-TERM PLANNING

Year	General Inflation (%)	Year	Fuel oil Inflation (%)	Year	Coal Inflation (%)
1981-82	12	1981-82	14	1981-82	15
1983-84	10	1983-85	12	1983-84	13
1985-86	9	1986-2000	8.5	1985-86	10
1987-2000	8			1987-2000	9

TABLE 2-2. ASSUMED ESCALATION RATES FOR COST OF ELECTRICITY, ADIPIC ACID AND DBA

Year	C.O.E. Escalation (%)	Year	Adipic acid and DBA Escalation (%)
1981-82	14.3	1981-82	13.5
1983-84	12.3	1983-84	11.5
1985-86	9.8	85	11.3
1987-2000	8.8	86	8.6
		1987-2000	8.4

The cost of adipic acid and dibasic acid have been assumed to be tied to the cost of petroleum (fuel oil). However, there is a capital component in addition to the raw material and transportation charges. Since this breakdown is not known, 75 percent of the cost of the buffers were assumed to escalate by the fuel oil inflation rate and the remaining 25 percent of the cost by the general inflation rate. The assumed escalation rates for adipic acid and DBA are presented in Table 2-2.

2.2 OPTION 1 - INCREASED LIQUID-TO-GAS RATIO

The first option considered is one in which the L/G is raised from ∿40 gal/1000 acf to ∿80 in the tray towers at full load conditions. This requires an additional pump, a revised pump discharge manifold, additional capacity in the slurry header to the scrubbing zone, and additional distribution headers and slurry feed nozzles for each of the two modules. The installed costs for this option and first year operating and maintenance costs are presented in Table 2-3.

Capital Costs

The total capital investment is estimated to be $615K in mid-1981 dollars. The pump and motor costs were obtained from Denver Equipment and Westinghouse, respectively. City Utilities obtained an estimate for an installed header system of $320K from a local contractor. This includes foundations and installation of the pumps. City Utilities estimates about $50K for electrical work associated with pump installation. Their analysis indicates that an additional motor control system is not required. C.U. factors of 8 percent for engineering and 8.6 percent for overhead were applied. This assumes that the specifications and evaluation would be performed by C.U. directly rather than employing an A&E for this small job.

Since the $65K was obtained in mid-1981, the 1982 costs were escalated by 6 percent yielding $652K. Assuming that one module would be modified in 1982 and one in 1983, the capital investment would be $326K in 1982 and $366K in 1983 (1.12 x 326K).

Operating and Maintenance

The first year maintenance costs are estimated to be $25K. This is based on an estimate of 8 percent per year of the direct capital investment for equipment in slurry service (Computerized Shawnee Lime/Limestone Scrubbing

TABLE 2-3. ESTIMATED CAPITAL INVESTMENT AND MID-1981 O&M COSTS FOR OPTION L (HIGHER L/G)

CAPITAL INVESTMENT	
Pump Costs	
Direct Capital	
Pumps - 2 @ $41,000[1]	$ 82,000
Motors - 2 @ $25,000[2]	50,000
Starters, drives, wire	18,000
Freight	4,000
Total	$154,000
Materials and Installation for Risers, Distribution Headers, Nozzles, Pump	
Foundation and installation of pumps[3]	320,000
Installation of Electricals[4]	50,000
Total Installed Cost	524,000
Other Indirect Costs	
Engineering (8% of installed cost)[5]	42,000
Overhead (8.6% of installed cost plus Engineering)[5]	49,000
TOTAL CAPITAL INVESTMENT	$615,000
OPERATING AND MAINTENANCE (First Year)	
Maintenance (8% of direct capital)[6] (.08 x ∿$310,000)	$ 25,000
Operation (electrical requirement for 2 additional pump drawing 50 amps each)	104,000
TOTAL FIRST YEAR O&M	$129,000

[1]Estimate from Denver Pump Co.

[2]Estimate from Westinghouse Electric Corp.

[3]Estimate obtained by C.U. from local contractor.

[4]Estimate from C.U.

[5]C.U. factors for Engineering and Overhead.

[6]Eight percent for maintenance from Computerized Shawnee Lime/Limestone Scrubbing Model Users Manual (March 1981).

Model Users Manual - March 1981). If half of the $320K header system installed is materials, then the maintenance would be

$$0.08(150 + 160K) = 25\ K/yr$$

Escalating this by 6 percent from mid-1981 dollars to 1982 dollars, the first year (1982) maintenance is estimated to be $27K. Only half of this would actually be spent in 1982 since only one module is assumed to be converted in 1982.

The increase in operating expenses is expected to be due to the increased electrical consumption by the additional pump. Assuming the FGD system operates for 10 months or 7200 hours per year and escalating to 1982 dollars, the operating cost would be

$$\frac{50\ \text{amps}}{} \left| \frac{(4160)(\text{volts})}{} \right| \frac{\text{watt}}{\text{volt-amp}} \left| \frac{(\sqrt{3})(0.8\ \text{power factor})}{} \right| \frac{\text{kW}}{1000\ \text{watts}}$$

$$\frac{7200\ \text{hrs}}{} \left| \frac{\$0.025}{\text{kWh}} \right| \frac{1.07}{} = \$56K$$

The 1983 operating expenses would be twice 56K (for the second pump) times 1.143 for escalation of cost of electricity from 1982 to 1983. The 1983 operating costs would be $127K for this option.

The results of the present worth analysis are shown in Table 2-4.

2.3 OPTION 1A - INCREASED PUMPING WITH CREDIT FOR CLASSIFIERS

C.U. has committed to installation of classifiers which should improve SO_2 removal as well as improve limestone grinding capabilities. Although an extensive study of SO_2 removal versus slurry flow rate has not been conducted, the improved limestone grinding should reduce the L/G required to meet the regulation. Our initial analysis shows that the increase in slurry flow

TABLE 2-4. OPTION 1 - INCREASED L/G IN TRAY TOWER

		Cost (1000 $)					
	Year	Capital	Maintenance	Operating	Total	Present Worth	Σ Present Worth
1982	1	326	13	56	395	395	395
1983	2	366	30	127	523	467	862
1984	3		33	143	176	143	1005
1985	4		37	160	197	145	1150
1986	5		40	176	216	146	1296
1987	6		43	193	236	147	1443
1988	7		47	210	257	148	1591
1989	8		51	228	279	149	1740
1990	9		55	248	303	149	1889
1991	10		59	270	329	150	2039
1992	11		64	294	358	151	2190
1993	12		69	320	389	152	2342
1994	13		75	348	423	153	2495
1995	14		80	379	459	154	2649
1996	15		87	412	499	155	2804

required would be about 60 percent (5/8) of that shown in Option 1. Note that this analysis is based on the shape of the SO_2 removal versus L/G curve being the same as the SO_2 removal versus adipic acid concentration. While this is sufficient for purposes of this study, there are significant technical uncertainties inherent in this estimate.

The capital cost for this option is assumed to be the same as Option 1. While a smaller pump could be installed, system flexibility would be reduced significantly. Also, the cost of installing the headers would not be reduced proportionately.

The cost savings considered here is the electrical operating cost. Additional pumping power requirements would be about 31 amps. The first year (1982) operating cost would be about $35K. Note this savings with the larger pumps would require some type of valve arrangement which can cause problems in slurry service.

The present worth analysis for this option is shown in Table 2-5.

2.4 OPTION 2 - ADIPIC ACID ADDITION

During testing with adipic acid between July 21 and August 10, 1981, an adipic acid feed rate of about 45 pounds per hour routinely resulted in 85 percent SO_2 removal in Module S-1 at full load conditions. Above 90 percent removal was achieved at lower loads. The average load over this period was 163 megawatts which is slightly higher than the 150 megawatt load estimated by C.U. for Unit 1 for 10 months of the year. This is offset somewhat by the slightly lower removal achieved in Module S-2. Additional removal is expected from S-2 when it is converted to a tray tower, and the higher SO_2 removal rate creates additional sludge which consumes additional adipic acid. Therefore, 45 pounds per hour feed rate seems to be a reasonable approximation of the average feed rate over the course of a year's operation.

TABLE 2-5. OPTION 1A - INC. PUMPING (CREDIT FOR CLASSIFIERS) (Revised)

	Year	Cost (1000 $)					
		Capital	Maintenance	Operating	Total	Present Worth	Σ Present Worth
1982	1	326	13	35	374	374	374
1983	2	366	15	80	461	412	786
1984	3		17	89	106	86	872
1985	4		18	100	118	87	959
1986	5		20	110	130	88	1047
1987	6		22	121	143	89	1136
1988	7		23	132	155	89	1225
1989	8		25	143	168	89	1314
1990	9		27	156	183	90	1404
1991	10		29	170	199	91	1495
1992	11		32	185	217	92	1587
1993	12		34	201	235	92	1679
1994	13		37	218	255	92	1771
1995	14		40	238	278	93	1864
1996	15		43	259	302	94	1958

Capital Costs

DuPont estimates that an adipic acid feed system could be installed for about $85K (letter from Harry Straw to Dale Hicks, September 3, 1981). This includes a 90,000 pound capacity silo (∿2.5 months of adipic acid storage), supports, air filter, star valve, blower and 60 feet of 4 inch conveying line. Actually, less conveyor would be necessary if the adipic acid were dissolved in a small mix tank and fed to the scrubbers in a solution. The mix tank and electrical work could add an additional $5K. C.U. engineering and overhead would bring the total cost to $106K and escalating this to 1982 dollars would make the capital expenditure $112K.

Operating and Maintenance

If the direct capital costs are assumed to be $50K, then the 1982 maintenance costs would be

$$(0.08)(\$50K) = \$4K$$

The operating cost would be the cost of adipic acid. Present cost of adipic acid is 59.5¢ per pound delivered to Springfield. A year's operating cost is computed to be:

$$\frac{45 \text{ lb adipic acid}}{\text{hr}} \left| \frac{7200 \text{ hr}}{\text{yr}} \right| \frac{\$0.595}{\text{lb adipic acid}} = \$193 \text{ K/yr}$$

In addition, one charge of adipic acid may be required each year. About 5000 pounds of adipic acid ($3K) is required to charge the system to 500 ppm. The total is therefore $196K. Escalating this from mid-1981 to 1982 dollars yields $209K.

Note that with adipic acid the system can be run with higher limestone utilization. However, no credit has been assumed since the classifiers should

also improve utilization. Further benefit with both classifiers and adipic acid could occur, but the decreased limestone consumption has not been quantified as yet.

Table 2-6 presents the present worth analysis of Option 2.

2.5 OPTION 2A - ADIPIC ACID WITH SO_2 REMOVAL CREDIT FOR CLASSIFIERS

The use of limestone classifiers should provide a finer grind of limestone which should improve dissolution of limestone in the tray tower which, in turn, should improve SO_2 removal efficiency. Pilot plant tests at RTP indicate that the SO_2 removal could improve from the 68-70 percent level up to about 80 percent. If this actually occurs, the amount of adipic acid consumed could be reduced to about 28 pounds/hour which would lower the 1982 operating costs to about $132K. Note that this reduction is based on mass transfer calculations and not actual pilot or field data. However, the shape of the SO_2 removal versus adipic acid concentration is fairly well defined which lends credence to the lower adipic acid consumption reported.

Table 2-7 shows the present worth analysis for Option 2A. No changes have been assumed for the capital or maintenance figures from Option 2.

2.6 OPTION 3 - DIBASIC ACID (DBA) ADDITION

DBA has been tested at EPA's RTP pilot plant and at the SWPP scrubbers in Springfield. Pilot plant testing has shown the DBA consumption to be about 20 percent higher than adipic acid consumption for equivalent FGD system performance. Testing at Springfield from September 12 through September 24 showed the actual DBA consumption to be about one-third higher than with adipic at similar load conditions.

TABLE 2-6. OPTION 2 - AA ADDITION (NO CREDIT FOR CLASSIFIERS) (Revised)

		Cost (1000 $)					
	Year	Capital	Maintenance	Operating	Total	Present Worth	Σ Present Worth
1982	1	112	4	209	325	325	325
1983	2		5	237	242	216	541
1984	3		5	264	269	218	759
1985	4		6	295	301	222	981
1986	5		6	328	334	226	1208
1987	6		7	356	363	225	1433
1988	7		7	386	393	226	1659
1989	8		8	418	426	227	1886
1990	9		9	453	462	228	2114
1991	10		9	492	501	229	2343
1992	11		10	533	543	230	2573
1993	12		11	578	589	231	2804
1994	13		12	626	638	231	3035
1995	14		13	679	692	232	3267
1996	15		14	736	750	233	3500

TABLE 2-7. OPTION 2A - AA ADDITION (CREDIT FOR CLASSIFIERS)

	Year	Cost (1000 $)					
		Capital	Maintenance	Operating	Total	Present Worth	Σ Present Worth
1982	1	112	4	132	282	288	288
1983	2		5	150	155	138	426
1984	3		5	167	172	140	566
1985	4		6	186	192	142	708
1986	5		6	207	213	144	852
1987	6		7	225	232	144	996
1988	7		7	244	251	144	1140
1989	8		8	265	273	145	1285
1990	9		9	287	296	146	1431
1991	10		9	311	320	146	1577
1992	11		10	337	347	147	1724
1993	12		11	365	376	147	1871
1994	13		12	396	408	148	2019
1995	14		13	429	442	148	2167
1996	15		14	465	479	149	2316

Capital Costs

The DBA feed system has not been designed and costed as yet. However, the system should be more simple than the adipic feed system since no solids handling equipment is required. An insulated 25,000 gallon tank should supply the storage capacity needed. External heating with steam or electricity will be required to keep solids from crystallizing but the energy consumption should be low. A reasonable assumption is that the DBA feed system will cost the same as the adipic acid feed system, $112K in 1982.

Operating and Maintenance

The maintenance is assumed to be the same ($4K in 1982) as the adipic acid option since the direct capital cost is assumed to be the same.

The operating cost will be primarily the cost of DBA. The feed rate of DBA is 60 pounds per hour (33 percent higher than adipic acid rate). The delivered cost of DBA as a 20 percent solution from Monsanto will be about $0.30 per pound which converts to an annual cost of 130K. One charge of DBA will cost about $2K so the total cost in mid-1981 dollars is $132K. Escalated to 1982 dollars this becomes $141K.

Table 2-8 shows the present worth analysis for Option 3.

2.7 OPTION 3A - DBA WITH CREDIT FOR CLASSIFIERS

The amount of DBA may be reduced because of the addition of classifiers. If the reduction is the same percentage as that assumed for adipic acid, the DBA rate would become

$$60\left(\frac{5}{8}\right) = 38 \text{ lb/hr}$$

This corresponds to $82 K/yr or $84 K/yr total if one charge to 500 ppm of DBA is assumed per year. Escalated to 1982 costs this becomes $90 K/yr.

TABLE 2-8. OPTION 3 - DBA (NO CREDIT FOR CLASSIFIERS)

		Cost (1000 $)					
	Year	Capital	Maintenance	Operating	Total	Present Worth	Σ Present Worth
1982	1	112	4	141	257	257	257
1983	2		5	160	165	148	405
1984	3		5	178	183	149	554
1985	4		6	198	204	149	703
1986	5		6	215	221	149	852
1987	6		7	233	240	149	1001
1988	7		7	253	260	149	1150
1989	8		8	274	282	150	1300
1990	9		9	297	306	151	1451
1991	10		9	322	331	151	1602
1992	11		10	349	359	152	1754
1993	12		11	378	389	152	1906
1994	13		12	410	422	152	2058
1995	14		13	444	457	153	2211
1996	15		14	482	496	154	2365

The present worth analysis for Option 3A is shown in Table 2-9.

2.8 OPTION 4 - SPRAY TOWER

UOP has proposed converting the two modules at Southwest to spray towers. There are some technical concerns, the main one being the high gas velocity through the towers (∿13 fps at full load). The high gas velocity can cause carryover problems and mist eliminator operating difficulties. Although this would not be the option chosen based on technical considerations, the spray tower option has been included here for completeness.

Capital Costs

UOP has estimated $900K to convert both modules to spray towers. This did include installation of new headers but did not include new pumps. Although slightly larger pumps and motors would be required for the spray tower option, the costs obtained for Option 1 will be used as an estimate here. The cost of new pumps and motors delivered to Springfield has been estimated to be $154K. The electrical work is estimated to be $50K and about $15K is estimated for installation of pumps and motors including foundations. The total installed cost is therefore $\$1.11 \times 10^6$. Assuming that the UOP cost includes engineering, only the 8.6 percent C.U. overhead would have to be applied bringing the total to $\$1.22 \times 10^6$. If one module is converted in 1982 and one in 1983, the capital investment for these years would be $644K and $721K, respectively.

Operating and Maintenance

According to UOP, much of the investment cost is installation due to the more involved header and nozzle arrangement in the spray tower. Since we do not have the actual breakdown for direct capital equipment, the maintenance cost is assumed to be the same as in Option 1.

UOP estimates that the L/G should be about 100 gal/1000 acf for this spray tower application. This means that the increase in L/G will be 50 percent

TABLE 2-9. OPTION 3A - DBA (CREDIT FOR CLASSIFIERS)

		Cost (1000 $)					
	Year	Capital	Maintenance	Operating	Total	Present Worth	Σ Present Worth
1982	1	112	4	90	206	206	206
1983	2		5	102	107	96	302
1984	3		5	114	119	96	398
1985	4		6	127	133	98	496
1986	5		6	138	144	98	594
1987	6		7	149	156	97	691
1988	7		7	162	169	97	788
1989	8		8	176	184	98	886
1990	9		9	190	199	98	984
1991	10		9	206	215	98	1082
1992	11		10	224	234	99	1181
1993	12		11	242	253	99	1280
1994	13		12	263	275	100	1380
1995	14		13	285	298	100	1480
1996	15		14	309	323	101	1581

higher than that in Option 1 which translates directly to a 50 percent higher increase in electrical consumption for the pumps. The 1982 operating cost for one module would be about $83,000.

The present worth analysis for the spray tower option is presented in Table 2-10.

TABLE 2-10. OPTION 4 - SPRAY TOWER MODIFICATION

		Cost (1000 $)					
	Year	Capital	Maintenance	Operating	Total	Present Worth	Σ Present Worth
1982	1	644	13	83	740	740	740
1983	2	721	30	190	941	840	1580
1984	3		33	213	246	200	1780
1985	4		37	239	276	204	1984
1986	5		40	263	303	205	2189
1987	6		43	288	331	206	2395
1988	7		47	314	361	208	2603
1989	8		51	341	392	209	2812
1990	9		55	372	427	211	3023
1991	10		59	404	463	211	3234
1992	11		64	440	504	213	3447
1993	12		69	479	548	214	3661
1994	13		75	521	596	216	3877
1995	14		80	566	646	217	4094
1996	15		87	616	703	218	4312

GENETICS ASSAY NOS. 6045-6048
LBI SAFETY NOS. 7383-7386

APPENDIX E

MUTAGENICITY EVALUATION OF SOLID FGD SLUDGE SAMPLES IN THE EPA LEVEL 1 AMES SALMONELLA/MICROSOME PLATE TEST

FINAL REPORT

SUBMITTED TO:

RADIAN CORPORATION
8501 MO-PAC BOULEVARD
P.O. BOX 9948
AUSTIN, TEXAS 78766-0948

SUBMITTED BY:

LITTON BIONETICS, INC.
5516 NICHOLSON LANE
KENSINGTON, MARYLAND 20895

LBI PROJECT NO. 20993

REPORT DATE: JANUARY 1982

PREFACE

This assay conforms to the standard EPA Level 1 procedure for the Ames Salmonella/microsome mutagenesis assay as described in "IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests"[1]. The data were evaluated and formatted as recommended in "Level 1 Biological Testing Assessment and Data Formatting"[2].

The Ames Salmonella/microsome mutagenesis assay has been shown to be a sensitive method for detecting mutagenic activity for a variety of chemicals representing various chemical classes[3]. This assay is one of several recommended by EPA to identify, categorize and rank the pollutant potential of influent and effluent streams from industrial and energy-producing processes. This assay has been well validated with a wide range of positive and negative control chemicals and complex environmental samples.

All procedures and documents pertaining to the receipt, storage, preparation, testing and evaluation of the test material shall conform to Litton Bionetics, Inc. standard operating procedures and the Good Laboratory Practices Regulations of 1979. Deviations from standard procedure shall be fully documented and noted in the report.

All test and control results in this report are supported by fully documented raw data which are permanently maintained in the files of the Department of Molecular Toxicology or in the archives of Litton Bionetics, Inc., 5516 Nicholson Lane, Kensington, Maryland 20895. Copies of raw data will be supplied to the sponsor upon request.

TABLE OF CONTENTS

		Page No.
	PREFACE	i
I.	SUMMARY	1
II.	OBJECTIVE	2
III.	TEST MATERIAL	3
	A. Description	3
	B. Handling and Preparation	3
IV.	MATERIALS	5
	A. Indicator Microorganisms	6
	B. Media	6
	C. Activation System	6
	1. S9 Homogenate	6
	2. S9 Mix	6
V.	EXPERIMENTAL DESIGN	7
	A. Dose Selection	7
	B. Mutagenicity Test	7
	1. Nonactivation Assay	7
	2. Activation Assay	8
	C. Control Compounds	8
	D. Recording and Presenting Data	9
VI.	RESULTS	11
	A. Interpretations	11
	1. Sample #1, Solid FGD Sludge	11
	2. Sample #2, Solid FGD Sludge	12
	3. Sample #4, Solid FGD Sludge	12
	4. Sample #5, DBA-FGD Sludge	13
	B. Tables	13
VII.	ASSAY ACCEPTANCE AND EVALUATION CRITERIA	25
	A. Surviving Populations	25
	B. Dose-Response Phenomena	26
	C. Control Tests	26
	D. Evaluation Criteria for Ames Assay	26
	1. Strains TA-1535 and TA-1537	27
	2. Strains TA-98 and TA-100	27
	3. Pattern	27
	4. Reproducibility	27

TABLE OF CONTENTS (Continued)

E. Relation Between Mutagenicity and Carcinogenicity 28
F. Criteria for Ranking Samples in the Ames Assay . . 28

VIII. REFERENCES 30

I. SUMMARY

The four FGD Sludge samples (Nos. 1, 2, 4 and 5) supplied by the Radian Corporation were evaluated for their genetic activity in the EPA Level 1 Ames *Salmonella* mutagenesis assay in the presence and absence of a metabolic activation system. The samples were assayed directly in their solid forms and after extraction with water.

Neither the solid forms nor the aqueous leachate forms of the four samples exhibited genetic activity in any of the assays conducted in this evaluation. In all cases, the minimum effective concentration (MEC) was greater than the maximum applicable dose (MAD) of 5 mg per plate for the solid forms of the samples and 200 µl per plate for the aqueous leachates of the samples. Therefore, the mutagenic activity of these samples were evaluated as nondetectable (ND) according to the evaluation criteria developed in the EPA Level 1 manual for the Ames *Salmonella* mutagenesis assay.[1]

Submitted by:
Study Director

D.R. Jagannath 1/29/82

D.R. Jagannath, Ph.D.
Section Chief,
Submammalian Genetics,
Department of Molecular Toxicology

Date

Reviewed by:

David J. Brusick 2/1/82

David J. Brusick, Ph.D.
Director,
Department of Molecular Toxicology

Date

II. OBJECTIVE

The objective of this study was to determine and rank the genetic activity of four solid FGD sludge samples in the Ames Salmonella mutagenesis assay with and without the addition of mammalian metabolic activation preparations. The mutagenicity of the samples; identified as Sample #1 Solid FGD sludge (natural oxidation with flyash and soil), Sample #2 Solid FGD sludge (natural oxidation with flyash, soil and adipic acid), Sample #4 Solid FGD sludge (forced oxidation with flyash, soil and adipic acid), and Sample #5 DBA-FGD solids (with flyash, soil and diabasic acid); was evaluated by testing both the solid form of the test material and aqueous leachates of the samples. The genetic activity of a sample was measured in these assays by its ability to revert the Salmonella indicator strains from histidine dependence to histidine independence. The degree of genetic activity of a sample was reflected in the number of revertants that were observed on the histidine-free medium. Standard EPA Level 1 mutagenicity evaluation criteria for the Ames mutagenesis assay were used to rank the mutagenic potential of each test material.

III. TEST MATERIAL

A. Description

Four samples were supplied by Radian Corporation, Austin, Texas. The samples were assigned LBI safety numbers and LBI assay numbers upon receipt. The Radian code numbers, sample identification, LBI safety numbers and LBI assay numbers are as follows:

Radian Corp. Code	Sample Identification	LBI Safety No.	LBI Assay No.
Sample #1	Solid FGD Sludge (natural oxidation with flyash and soil)	7383	6045
Sample #2	Solid FGD Sludge (natural oxidation with flyash, soil and adipic acid)	7384	6046
Sample #4	Solid FGD Sludge (forced oxidation with flyash, soil and adipic acid)	7385	6047
Sample #5	DBA-FGD Solids (with flyash, soil and dibasic acid)	7386	6048

Sample #1 was received as a brown/gray granular particulate with white flakes. Sample #2 was a fine, dark brown/gray powder. Sample #4 consisted of sand-like particles of a light tan color. Sample #5 was a coarse, variable-sized particulate of black and gray color.

No information on sampling parameters was provided.

B. Handling and Preparation

The test materials were received at LBI on November 30, 1981. The samples were individually packed in zip-lock plastic bags and placed inside a cardboard carton. The samples were received intact and were stored at +4°C in the dark until used.

Before testing the solid samples in the Salmonella assay, the samples were decontaminated by incubating the samples with acetone. Approximately,

1 to 2 gm of the samples were were mixed with 10 ml of acetone and incubated overnight at 45°C on a heating block (to evaporate the acetone). The acetone treated solids were then used in the assays.

Aqueous leachates of the samples were prepared by shaking 30 gm of each sample with 120 ml of sterile deionized water at 200 rpm for 48 hours. The suspensions were allowed to settled, and the supernatants were decanted into 50 ml conical centrifuge tubes and centrifuged for 20 minutes at 850 x g. The leachates were then filtered through 0.45 μg Nalgene filters and stored in sterile tissue culture flasks at +4°C in the dark.

IV. MATERIALS

A. Indicator Microorganisms

The *Salmonella typhimurium* strains used in this assay were obtained from Dr. Bruce Ames, University of California at Berkeley.[4-9] The following four strains were used.

Strain Designation	Gene Affected	Additional Mutations			Mutation Type Detected
		Repair	LPS	R Factor	
TA-1535	his G	Δ uvr B	rfa	-	Base-pair substitution
TA-1537	his C	Δ uvr B	rfa	-	Frameshift
TA-98	his D	Δ uvr B	rfa	pKM101	Frameshift
TA-100	his G	Δ uvr B	rfa	pKM101	Base-pair substitution

All the above strains have, in addition to the mutation in the histidine operon, mutation (rfa-) that leads to defective lipopolysaccharide coat, a deletion that covers genes involved in the synthesis of vitamin biotin (bio-) and in the repair of ultraviolet (uv) - induced DNA damage (uvrB-). The rfa- mutation makes the strains more permeable to many large molecules. The uvrB- mutation decreases repair of some types of chemically or physically damaged DNA and thereby enhances the strain's sensitivity to some mutagenic agents. The resistant transfer factor plasmid (R factor) pKM101 in TA-98 and TA-100 is believed to cause an increase in error-prone DNA repair that leads to many more mutations for a given dose of most mutagens.[8] In addition, plasmid pKM101 confers resistance to the antibiotic ampicillin, which is a convenient marker to detect the presence of plasmid in the cells.

All indicator strains were kept at 4°C on minimal medium plates supplemented with a trace of biotin and an excess of histidine. In addition, the plates with plasmid-carrying strains contained ampicillin (25 μg/ml) to

ensure stable maintenance of plasmid pKM101. New stock culture plates were made as often as necessary from the frozen master cultures or from single colony reisolates that were checked for their genotypic characteristics (his, rfa, uvrB, and bio) and for the presence of plasmid. For each experiment, an inoculum from the stock culture plates was grown overnight at 37°C in nutrient broth (Oxoid CM67) and used.

B. Media

The bacterial strains were cultured in Oxoid Media #2 (Nutrient Broth). The selective medium was Vogen Bonner Medium E with 2% glucose.[10] The overlay agar consisted of 0.6% purified agar with 0.05 mM histidine, 0.05 mM biotin and 0.1M NaCl according to the methods of Ames et al.[9]

C. Activation System

1. S9 Homogenate

A 9,000 x g supernatant prepared from Sprague-Dawley adult male rat liver induced by Aroclor 1254 (Ames et al.[9]) was purchased commercially and used in these assays.

2. S9 Mix

S9 mix used in these assays consisted of the following components:

Components	Concentration per Milliliter S9 Mix
NADP (sodium salt)	4 µmoles
D-glucose-6-phosphate	5 µmoles
$MgCl_2$	8 µmoles
KCl	33 µmoles
Sodium phosphate buffer pH 7.4	100 µmoles
Organ homogenate from rat liver (S9 fraction)	100 µliters

V. EXPERIMENTAL DESIGN

A. Dosage Selection

Test strategy and dose selection depend upon sample type and sample availability. The Level 1 manual[1] recommends solids to be initially tested at the maximum applicable dose (MAD) of 5 mg per plate and at lower concentrations of 2.5, 1, 0.5, 0.1 and 0.05 mg per plate. Liquids are tested initially at the MAD of 200 µl per plate, and at lower concentrations of 100, 50 and 10 µl per plate. Samples are retested over a narrower range of concentrations with strains showing positive results initially. Alternate doses are employed if sample size is limiting or at the direction of the sponsor.

The solid samples were assayed at the single concentration of 5 mg per plate, the maximum applicable dose for solids. The aqueous leachates were tested at the recommended four concentrations for liquids of 200, 10, 50 and 10 µl per plate.

B. Mutagenicity Testing

The procedure used was based on the paper published by Ames *et. al.*[9] and was performed as follows:

1. Nonactivation Assay

To a sterile 13 x 100 mm test tube placed in a 43°C water bath the following was added in order:

- 2.00 ml of 0.6% agar containing 0.05 mM histidine and 0.05 mM biotin.

- 0.01 ml to 0.2 ml of the aqueous leachate, or 5 mg of the solid, to give the appropriate dose.

- 0.1 ml to 0.2 ml of indicator organism(s).

- 0.50 ml of 0.2M phosphate buffer, pH 7.4.

This mixture was swirled gently and then poured onto minimal agar plates (see IV B, Media). After the top agar had set, the plates were incubated at 37°C for approximately 2 days. The number of his+ revertant colonies growing on the plates were counted with an automatic colony counter and recorded.

2. Activation Assay

The activation assay was run concurrently with the nonactivation assay. The only difference was the addition of 0.5 ml of S9 mix (see IV C, Activation System) to the tubes in place of 0.5 ml of phosphate buffer which was added in nonactivation assays. All other details were similar to the procedure for nonactivation assays.

A detailed flow diagram for the plate incorporation assay is provided in Figure 1.

C. Control Compounds

A negative control consisting of the solvent used for the test material was also assayed concurrently with the test material. For negative controls, step 'b' of Nonactivation Assays was replaced by 0.05 ml of the solvent. The negative controls were employed for each indicator strain and were performed in the absence and presence of S9 mix. The solvent used to prepare the stock solution of the test material is given in the Results section of this report. All dilutions of the test material were made using this solvent. The amount of solvent used was equal to the maximum volume used to give the appropriate test dose.

AMES ASSAY [PLATE INCORPORATION METHOD]

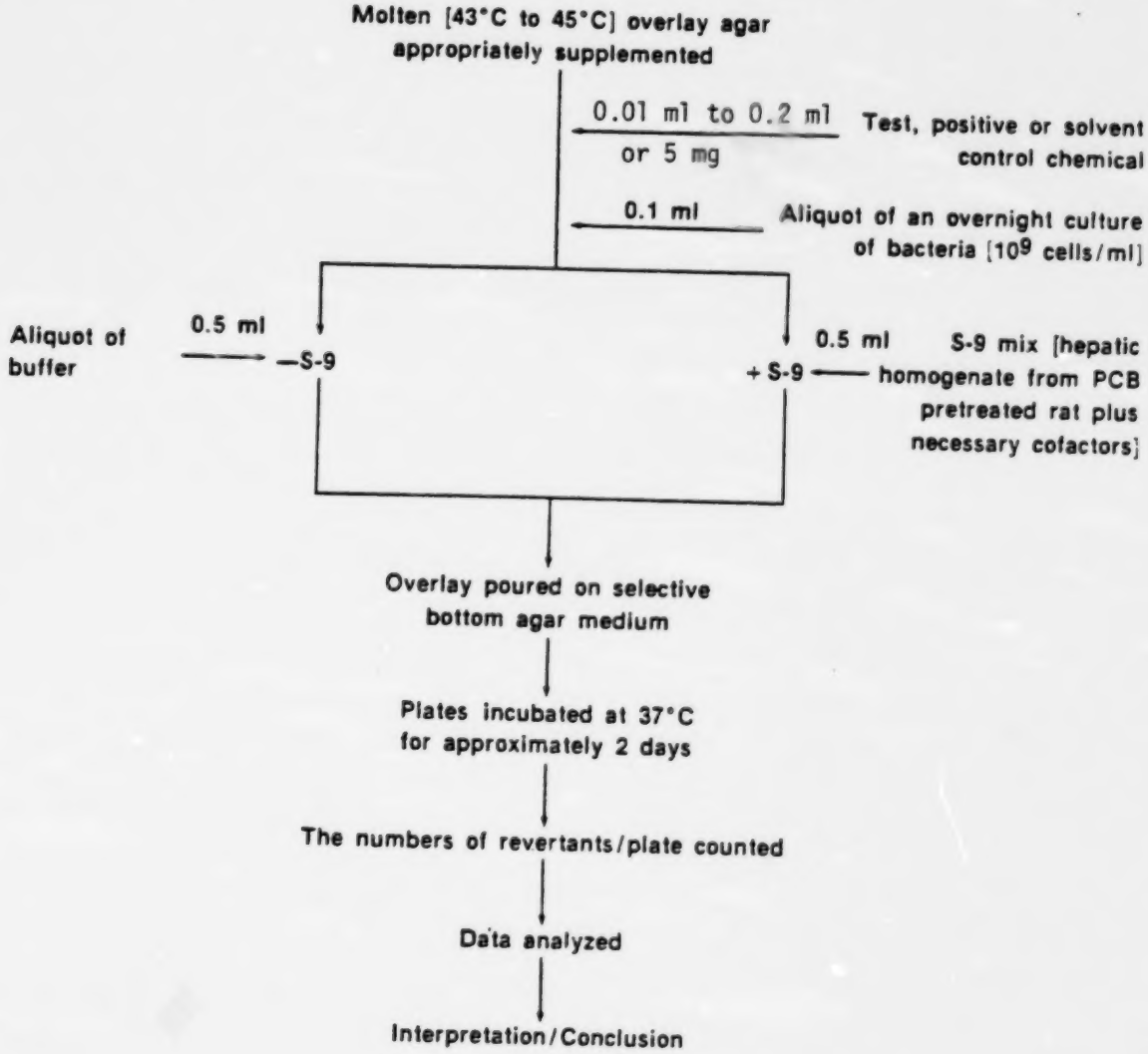


Figure 1 AMES SALMONELLA/MICROSOME MUTAGENESIS ASSAY

Specific positive control compounds known to revert each strain were also used and assayed concurrently with the test material. The concentrations and specificities of these compounds to specific strains are given in the following table:

Assay	Chemical	Solvent	Concentration per plate (μg)	Salmonella Strains
Nonactivation	Sodium azide	Water	10.0	TA-1535, TA-100
	2-Nitrofluorene (NF)	Dimethyl-sulfoxide	10.0	TA-98
	9-aminoacridine (9AA)	Ethanol	50.0	TA-1537
Activation	2-anthramine (ANTH)	Dimethyl-sulfoxide	2.5	For all strains

D. Recording and Presenting Data

The number of colonies on each plate were counted and recorded on printed forms. These raw data were analyzed in a computer program and reported on a printout. The results are presented as revertants per plate for each indicator strain employed in the assay. The positive and solvent controls are provided as reference points.

VI. RESULTS

A. Interpretation

The four samples, FGD sludge Samples #1, 2, 4, and 5, received from Radian Corporation were leached in sterile deionized water. Thirty gm of each sample were added to 120 ml of sterile deionized water and shaken for 48 hours at 200 rpm. After incubation , the leachate was decanted and remaining solids were removed by centrifugation. The supernatant was then fiter sterilized by passing the liquid through 0.45 fiter. The resulting leachate and the unextracted solid were tested for their genetic activity in the EPA Level 1 Ames Salmonella assay in the presence and absence of a metabolic activation system.

The solid samples were assayed at a single concentration of 5.0 mg plate and the leachates were assayed at four concentrations of 10, 50, 100 and 200 µl per plate. Results of the Ames Salmonella assays are presented in Tables 1 through 11.

Solvent control and positive control values were within acceptable ranges. These results achieved assay acceptance criteria and provided confidence in the assumptions that the recorded data represented typical responses to the test material.

1. Sample #1, Solid FGD Sludge

The results of the assays conducted on the FGD Sample #1 before extracting in water were negative in the presence and absence of a metabolic activation system (Table 1). The minimum effective concentration (MEC) was greater than 5 mg/plate which permitted the sample to be ranked as having nondetectable (ND) mutagenic activity.

The results of the assays conducted on the FGD Sample #1 leachate were also negative both in the activation and nonactivation assays (Table 2). The sample was evaluated as having nondetectable (ND) mutagenic activity sed upon a MEC greater than 200 µl/ml.

2. Sample #2, Solid FGD Sludge

The results of the assays conducted on the solid as well as aqueous leachate of the FGD Sludge sample #2 were negative in the presence and absence of a metabolic activation system (Tables 3 and 4). The test with the leachate was repeated with strains TA-98 and TA-100 in the presence of the metabolic activation system because of the low number of revertants observed at various test doses in the initial assay. These repeat tests were also negative (Table 5).

Both forms of sample #2 were ranked as having nondetectable (ND) mutagenic activity. These evaluations were based upon MEC values greater than 5 mg/plate for the solid form and greater than 200 µl/plate for the aqueous leachate of the sample.

3. Sample #4, Solid FGD Sludge

The results of the assays conducted on the solid (Table 6) as well as aqueous leachate (Table 7) of the FGD Sludge Sample #4 were negative in the activation and nonactivation assays. The strain TA-98 exhibited increased number of revertants at the 200 µl/plate dose with the leachate but the increases were considered not significant since no dose-related response was observed. The test with the leachate was repeated with strains TA-1537 and TA-100 in the nonactivation assays because of the low number of revertants observed at various test doses in the initial assay. The repeat tests were also negative (Table 8).

The mutagenic response of sample #4 was basically similar to that seen with samples #1 and #2. Both the solid form and the aqueous leachate of sample #4 were ranked as having nondetectable (ND) mutagenic activity based upon MEC values greater than 5 mg/plate for the solid and 200 µl/plate for the leachate.

4. Sample #5, DBA-FGD Solid

The results of the assays conducted on both the solid (Table 9) and the aqueous leachate (Table 10) of the FGD Sludge sample #5 were negative in the activation and nonactivation assays. The assays with the leachate were repeated with all the strains with both activation and nonactivation, since a few contaminating microbial colonies were observed on the test dose plates. These repeat tests performed on the leachate were all negative (Table 11). Since no MEC values were observed, the two forms of sample #5 were ranked as having nondetectable (ND) mutagenic activity.

B. Tables

This report is based on the data provided in Tables 1 through 11.

RESULTS

TABLE 1

A. NAME OR CODE DESIGNATION OF THE TEST COMPOUND: SAMPLE#1 SOLID FGD SLUDGE (SOLID)
B. SOLVENT: NONE
C. TEST INITIATION DATES: 12/31/81
D. TEST COMPLETION DATE: 01/04/82
E. S-9 LOT#: REG053
NOTE: CONCENTRATIONS ARE GIVEN IN MILLIGRAMS PER PLATE

TEST	SPECIES	TISSUE	REVERTANTS PER PLATE TA-1535 1	TA-1535 2	TA-1535 3	TA-1537 1	TA-1537 2	TA-1537 3	TA-98 1	TA-98 2	TA-98 3	TA-100 1	TA-100 2	TA-100 3
NONACTIVATION														
NEGATIVE CONTROL	---	---	17	16	11	12	13	10	45	33	45	120	123	151
POSITIVE CONTROL**	---	---	849	892	1035	348	366	401	900	872	898	689	657	607
TEST COMPOUND 5.00000 MG	---	---	14	16	11	7	2	6	52	43	43	108	134	155
ACTIVATION														
NEGATIVE CONTROL	RAT	LIVER	10	13	13	15	13	18	48	53	56	126	173	136
POSITIVE CONTROL***	RAT	LIVER	426	410	432	225	233	213	1425	1526	1561	1659	1644	1900
TEST COMPOUND 5.00000 MG	RAT	LIVER	13	13	13	14	9	9	55	63	60	168	153	159

**

TA-1535	SODIUM AZIDE	10 UG/PLATE
TA-1537	9-AMINOACRIDINE	50 UG/PLATE
TA-98	2-NITROFLUORENE	10 UG/PLATE
TA-100	SODIUM AZIDE	10 UG/PLATE

***

TA-1535	2-ANTHRAMINE	2.5 UG/PLATE
TA-1537	2-ANTHRAMINE	2.5 UG/PLATE
TA-98	2-ANTHRAMINE	2.5 UG/PLATE
TA-100	2-ANTHRAMINE	2.5 UG/PLATE

RESULTS

TABLE 2

A. NAME OR CODE DESIGNATION OF THE TEST COMPOUND: SAMPLE#1 FGD SLUDGE (AQUEOUS LEACHATE)
B. SOLVENT: D.H2O
C. TEST INITIATION DATES: 12/30/81
D. TEST COMPLETION DATE: 01/04/82
E. S-9 LOT#: REG053
NOTE: CONCENTRATIONS ARE GIVEN IN MICROLITERS PER PLATE

TEST		SPECIES	TISSUE	REVERTANTS PER PLATE TA-1535 1	TA-1535 2	TA-1535 3	TA-1537 1	TA-1537 2	TA-1537 3	TA-98 1	TA-98 2	TA-98 3	TA-100 1	TA-100 2	TA-100 3
NONACTIVATION															
SOLVENT CONTROL		---	---	14	15		16	13		26	28		100	115	
POSITIVE CONTROL**		---	---	1082	1016		560	722		1025	1096		1467	1748	
TEST COMPOUND															
10.00	UL	---	---	28	26		17	33		38	30		112	122	
50.00	UL	---	---	41	43		20	23		38	32		104	108	
100.00	UL	---	---	21	35		21	21		36	38		113	123	
200.00	UL	---	---	36	32		25	22		35	37		131	117	
ACTIVATION															
SOLVENT CONTROL		RAT	LIVER	16	23		28	19		42	42		108	109	
POSITIVE CONTROL***		RAT	LIVER	395	421		253	286		1804	1849		2306	2297	
TEST COMPOUND															
10.00	UL	RAT	LIVER	14	19		20	34		29	36		102	132	
50.00	UL	RAT	LIVER	12	21		21	25		33	37		100	138	
100.00	UL	RAT	LIVER	17	19		26	32		34	44		124	122	
200.00	UL	RAT	LIVER	17	12		31	28		33	29		107	127	

**

TA-1535	SODIUM AZIDE	10 UG/PLATE
TA-1537	9-AMINOACRIDINE	50 UG/PLATE
TA-98	2-NITROFLUORENE	10 UG/PLATE
TA-100	SODIUM AZIDE	10 UG/PLATE
SOLVENT	200 UL/PLATE	

***

TA-1535	2-ANTHRAMINE	2.5 UG/PLATE
TA-1537	2-ANTHRAMINE	2.5 UG/PLATE
TA-98	2-ANTHRAMINE	2.5 UG/PLATE
TA-100	2-ANTHRAMINE	2.5 UG/PLATE

RESULTS

TABLE 3

A. NAME OR CODE DESIGNATION OF THE TEST COMPOUND: SAMPLE#2 SOLID FGD SLUDGE (SOLID)
B. SOLVENT: NONE
C. TEST INITIATION DATES: 12/31/81
D. TEST COMPLETION DATE: 01/04/82
E. S-9 LOT#: REG053
NOTE: CONCENTRATIONS ARE GIVEN IN MILLIGRAMS PER PLATE

TEST	SPECIES	TISSUE	REVERTANTS PER PLATE TA-1535 1	TA-1535 2	TA-1535 3	TA-1537 1	TA-1537 2	TA-1537 3	TA-98 1	TA-98 2	TA-98 3	TA-100 1	TA-100 2	TA-100 3
NONACTIVATION														
NEGATIVE CONTROL	---	---	17	16	11	12	13	10	45	33	45	120	123	151
POSITIVE CONTROL**	---	---	849	852	1035	348	366	401	900	872	898	689	657	687
TEST COMPOUND 5.00000 MG	---	---	9	16	14	3	1	2	42	41	38	75	123	125
ACTIVATION														
NEGATIVE CONTROL	RAT	LIVER	10	13	13	15	13	18	48	53	56	126	173	136
POSITIVE CONTROL***	RAT	LIVER	426	410	432	225	233	213	1425	1526	1561	1659	1644	1900
TEST COMPOUND 5.00000 MG	RAT	LIVER	11	11	20	5	6	3	57	61	58	120	116	126

**

TA-1535	SODIUM AZIDE	10 UG/PLATE
TA-1537	9-AMINOACRIDINE	50 UG/PLATE
TA-98	2-NITROFLUORENE	10 UG/PLATE
TA-100	SODIUM AZIDE	10 UG/PLATE

***

TA-1535	2-ANTHRAMINE	2.5 UG/PLATE
TA-1537	2-ANTHRAMINE	2.5 UG/PLATE
TA-98	2-ANTHRAMINE	2.5 UG/PLATE
TA-100	2-ANTHRAMINE	2.5 UG/PLATE

RESULTS

TABLE 4

A. NAME OR CODE DESIGNATION OF THE TEST COMPOUND: SAMPLE#2 SOLID FGD SLUDGE (AQUEOUS LEACHATE)
B. SOLVENT: D.H2O
C. TEST INITIATION DATES: 12/31/81
D. TEST COMPLETION DATE: 01/04/82
E. S-9 LOT#: REG053
NOTE: CONCENTRATIONS ARE GIVEN IN MICROLITERS PER PLATE

TEST		SPECIES	TISSUE	REVERTANTS PER PLATE TA-1535 1	TA-1535 2	TA-1535 3	TA-1537 1	TA-1537 2	TA-1537 3	TA-98 1	TA-98 2	TA-98 3	TA-100 1	TA-100 2	TA-100 3
NONACTIVATION															
SOLVENT CONTROL		---	---	16	20		10	11		40	43		114	114	
POSITIVE CONTROL**		---	---	1013	1111		348	266		1121	845		890	1387	
TEST COMPOUND															
10.00	UL	---	---	19	17		8	8		33	48		123	113	
50.00	UL	---	---	18	22		7	8		49	40		118	85	
100.00	UL	---	---	14	18		2	8		46	51		125	124	
200.00	UL	---	---	20	19		5	7		43	40		108	125	
ACTIVATION															
SOLVENT CONTROL		RAT	LIVER	12	13		13	15		25	28		103	124	
POSITIVE CONTROL***		RAT	LIVER	325	377		225	233		1467	1522		2352	2440	
TEST COMPOUND															
10.00	UL	RAT	LIVER	7	14		10	9		9	50		53	102	
50.00	UL	RAT	LIVER	9	20		7	12		16	59		52	100	
100.00	UL	RAT	LIVER	8	19		15	8		19	52		76	122	
200.00	UL	RAT	LIVER	20	18		10	14		34	52		80	120	

**

TA-1535	SODIUM AZIDE	10 UG/PLATE
TA-1537	9-AMINOACRIDINE	50 UG/PLATE
TA-98	2-NITROFLUORENE	10 UG/PLATE
TA-100	SODIUM AZIDE	10 UG/PLATE
SOLVENT	200 UL/PLATE	

***

TA-1535	2-ANTHRAMINE	2.5 UG/PLATE
TA-1537	2-ANTHRAMINE	2.5 UG/PLATE
TA-98	2-ANTHRAMINE	2.5 UG/PLATE
TA-100	2-ANTHRAMINE	2.5 UG/PLATE

RESULTS

TABLE 5

A. NAME OR CODE DESIGNATION OF THE TEST COMPOUND: SAMPLE#2 SOLID FGD SLUDGE (AQUEOUS LEACHATE)
B. SOLVENT: D.H2O
C. TEST INITIATION DATES: 01/06/82
D. TEST COMPLETION DATE: 01/11/82
E. S-9 LOT#: REG053
NOTE: CONCENTRATIONS ARE GIVEN IN MICROLITERS PER PLATE

TEST		SPECIES	TISSUE	REVERTANTS PER PLATE TA-98 1	TA-98 2	TA-98 3	TA-100 1	TA-100 2	TA-100 3
ACTIVATION									
SOLVENT CONTROL		RAT	LIVER	32	37		144	158	
POSITIVE CONTROL***		RAT	LIVER	1832	1845		1625	1655	
TEST COMPOUND									
10.00	UL	RAT	LIVER	22	29		75	87	
50.00	UL	RAT	LIVER	25	20		84	95	
100.00	UL	RAT	LIVER	18	23		89	93	
200.00	UL	RAT	LIVER	26	37		73	94	

**
TA-98 2-NITROFLUORENE 10 UG/PLATE
TA-100 SODIUM AZIDE 10 UG/PLATE
SOLVENT 200 UL/PLATE

***
TA-98 2-ANTHRAMINE 2.5 UG/PLATE
TA-100 2-ANTHRAMINE 2.5 UG/PLATE

RESULTS

TABLE 6

A. NAME OR CODE DESIGNATION OF THE TEST COMPOUND: SAMPLE#4 SOLID FGD SLUDGE (SOLID)
B. SOLVENT: NONE
C. TEST INITIATION DATES: 01/08/82
D. TEST COMPLETION DATE: 01/11/82
E. S-9 LOT#: REG053
NOTE: CONCENTRATIONS ARE GIVEN IN MICROGRAMS PER PLATE

TEST		SPECIES	TISSUE	REVERTANTS PER PLATE TA-1535 1	TA-1535 2	TA-1535 3	TA-1537 1	TA-1537 2	TA-1537 3	TA-98 1	TA-98 2	TA-98 3	TA-100 1	TA-100 2	TA-100 3
NONACTIVATION															
NEGATIVE CONTROL		---	---	17	14	15	13	14	12	40	44	49	107	124	141
POSITIVE CONTROL**		---	---	796	717	585	442	402	257	867	728	925	1067	1043	1053
TEST COMPOUND 5000.00	UG	---	---	15	14	13	23	15	26	33	29	37	113	127	142
ACTIVATION															
NEGATIVE CONTROL		RAT	LIVER	11	13	16	15	19	10	48	50	49	126	123	150
POSITIVE CONTROL***		RAT	LIVER	345	381	359	264	242	305	1259	1318	1489	1894	2005	2050
TEST COMPOUND 5000.00	UG	RAT	LIVER	13	18	13	15	23	19	32	34	60	114	146	142

**

TA-1535	SODIUM AZIDE	10 UG/PLATE
TA-1537	9-AMINOACRIDINE	50 UG/PLATE
TA-98	2-NITROFLUORENE	10 UG/PLATE
TA-100	SODIUM AZIDE	10 UG/PLATE

***

TA-1535	2-ANTHRAMINE	2.5 UG/PLATE
TA-1537	2-ANTHRAMINE	2.5 UG/PLATE
TA-98	2-ANTHRAMINE	2.5 UG/PLATE
TA-100	2-ANTHRAMINE	2.5 UG/PLATE

RESULTS

TABLE 7

A. NAME OR CODE DESIGNATION OF THE TEST COMPOUND: SAMPLE#4 SOLID FGD SLUDGE (AQUEOUS LEACHATE)
B. SOLVENT: D.H2O
C. TEST INITIATION DATES: 12/31/81
D. TEST COMPLETION DATE: 01/04/82
E. S-9 LOT#: REG053
NOTE: CONCENTRATIONS ARE GIVEN IN MICROLITERS PER PLATE

TEST		SPECIES	TISSUE	REVERTANTS PER PLATE TA-1535 1	TA-1535 2	TA-1535 3	TA-1537 1	TA-1537 2	TA-1537 3	TA-98 1	TA-98 2	TA-98 3	TA-100 1	TA-100 2	TA-100 3
NONACTIVATION															
SOLVENT CONTROL		---	---	16	20		10	11		40	43		114	114	
POSITIVE CONTROL**		---	---	1013	1111		348	366		1121	845		890	1387	
TEST COMPOUND															
10.00	UL	---	---	23	15		1	11		11	38		23	120	
50.00	UL	---	---	19	13		1	14		30	37		61	119	
100.00	UL	---	---	13	15		5	12		44	47		73	135	
200.00	UL	---	---	20	12		5	11		45	52		102	116	
ACTIVATION															
SOLVENT CONTROL		RAT	LIVER	12	13		13	15		25	20		103	124	
POSITIVE CONTROL***		RAT	LIVER	325	377		225	233		1467	1522		2352	2440	
TEST COMPOUND															
10.00	UL	RAT	LIVER	16	10		5	10		36	24		85	105	
50.00	UL	RAT	LIVER	13	6		10	13		46	39		117	115	
100.00	UL	RAT	LIVER	12	15		9	9		48	37		114	109	
200.00	UL	RAT	LIVER	9	9		15	16		53	49		106	108	

**

TA-1535	SODIUM AZIDE	10 UG/PLATE
TA-1537	9-AMINOACRIDINE	50 UG/PLATE
TA-98	2-NITROFLUORENE	10 UG/PLATE
TA-100	SODIUM AZIDE	10 UG/PLATE
SOLVENT	200 UL/PLATE	

***

TA-1535	2-ANTHRAMINE	2.5 UG/PLATE
TA-1537	2-ANTHRAMINE	2.5 UG/PLATE
TA-98	2-ANTHRAMINE	2.5 UG/PLATE
TA-100	2-ANTHRAMINE	2.5 UG/PLATE

RESULTS

TABLE 8

A. NAME OR CODE DESIGNATION OF THE TEST COMPOUND: SAMPLE#4 SOLID FGD SLUDGE (AQUEOUS LEACHATE)
B. SOLVENT: D.H20
C. TEST INITIATION DATES: 01/05/82
D. TEST COMPLETION DATE: 01/08/82
E. S-9 LOT#:
NOTE: CONCENTRATIONS ARE GIVEN IN MICROLITERS PER PLATE

TEST		SPECIES	TISSUE	REVERTANTS PER PLATE TA-1537 1	TA-1537 2	TA-1537 3	TA-100 1	TA-100 2	TA-100 3
NONACTIVATION									
SOLVENT CONTROL		---	---	5	7		119	131	
POSITIVE CONTROL**		---	---	374	390		1229	1318	
TEST COMPOUND									
10.00	UL	---	---	4	3		103	109	
50.00	UL	---	---	6	7		98	111	
100.00	UL	---	---	3	9		95	113	
200.00	UL	---	---	1	2		100	124	

**
TA-1537 9-AMINOACRIDINE 50 UG/PLATE
TA-100 SODIUM AZIDE 10 UG/PLATE
SOLVENT 200 UL/PLATE

RESULTS

TABLE 9

A. NAME OR CODE DESIGNATION OF THE TEST COMPOUND: SAMPLE#5 DBA-FGD SOLIDS (SOLID)
B. SOLVENT: NONE
C. TEST INITIATION DATES: 01/08/82
D. TEST COMPLETION DATE: 01/11/82
F. S-9 LOT#: REG053
NOTE: CONCENTRATIONS ARE GIVEN IN MICROGRAMS PER PLATE

TEST	SPECIES	TISSUE	REVERTANTS PER PLATE TA-1535 1	TA-1535 2	TA-1535 3	TA-1537 1	TA-1537 2	TA-1537 3	TA-98 1	TA-98 2	TA-98 3	TA-100 1	TA-100 2	TA-100 3
NONACTIVATION														
NEGATIVE CONTROL	---	---	17	14	15	13	14	12	40	44	49	107	124	141
POSITIVE CONTROL**	---	---	796	717	585	442	402	257	867	728	925	1067	1043	1053
TEST COMPOUND 5000.00 UG	---	---	21	10	13	23	24	25	34	34	53	93	136	117
ACTIVATION														
NEGATIVE CONTROL	RAT	LIVER	11	13	16	15	19	10	48	50	49	126	123	130
POSITIVE CONTROL***	RAT	LIVER	345	381	359	264	242	306	1259	1318	1489	1894	2005	2096
TEST COMPOUND 5000.00 UG	RAT	LIVER	19	13	13	22	16	18	44	46	51	155	123	139

**

TA-1535	SODIUM AZIDE	10 UG/PLATE
TA-1537	9-AMINOACRIDINE	50 UG/PLATE
TA-98	2-NITROFLUORENE	10 UG/PLATE
TA-100	SODIUM AZIDE	10 UG/PLATE

***

TA-1535	2-ANTHRAMINE	2.5 UG/PLATE
TA-1537	2-ANTHRAMINE	2.5 UG/PLATE
TA-98	2-ANTHRAMINE	2.5 UG/PLATE
TA-100	2-ANTHRAMINE	2.5 UG/PLATE

RESULTS

TABLE 10

A. NAME OR CODE DESIGNATION OF THE TEST COMPOUND: SAMPLE#5 DBA-FGD SOLIDS (AQUEOUS LEACHATE)
B. SOLVENT: D.H2O
C. TEST INITIATION DATES: 12/31/81
D. TEST COMPLETION DATE: 01/04/82
E. S-9 LOT#: REG053
NOTE: CONCENTRATIONS ARE GIVEN IN MICROLITERS PER PLATE

TEST		SPECIES	TISSUE	REVERTANTS PER PLATE TA-1535 1	TA-1535 2	TA-1535 3	TA-1537 1	TA-1537 2	TA-1537 3	TA-98 1	TA-98 2	TA-98 3	TA-100 1	TA-100 2	TA-100 3
NONACTIVATION															
SOLVENT CONTROL		---	---	16	20		10	11		40	43		114	114	
POSITIVE CONTROL**		---	---	1013	1111		348	366		1121	845		890	1387	
TEST COMPOUND															
10.00	UL	---	---	25	21		12	11		42	39		81	91	
50.00	UL	---	---	14	21		16	9		45	32		99	145	
100.00	UL	---	---	22	15		9	14		38	49		104	105	
200.00	UL	---	---	16	12		11	9		42	47		114	134	
ACTIVATION															
SOLVENT CONTROL		RAT	LIVER	12	13		13	15		25	20		103	124	
POSITIVE CONTROL***		RAT	LIVER	325	377		225	233		1467	1522		2352	2440	
TEST COMPOUND															
10.00	UL	RAT	LIVER	17	15		5	9		49	54		81	101	
50.00	UL	RAT	LIVER	14	18		9	19		44	47		93	83	
100.00	UL	RAT	LIVER	13	14		6	14		56	53		102	79	
200.00	UL	RAT	LIVER	20	14		8	10		46	43		83	91	

**

TA-1535	SODIUM AZIDE	10 UG/PLATE
TA-1537	9-AMINOACRIDINE	50 UG/PLATE
TA-98	2-NITROFLUORENE	10 UG/PLATE
TA-100	SODIUM AZIDE	10 UG/PLATE
SOLVENT	200 UL/PLATE	

***

TA-1535	2-ANTHRAMINE	2.5 UG/PLATE
TA-1537	2-ANTHRAMINE	2.5 UG/PLATE
TA-98	2-ANTHRAMINE	2.5 UG/PLATE
TA-100	2-ANTHRAMINE	2.5 UG/PLATE

RESULTS

TABLE 11

A. NAME OR CODE DESIGNATION OF THE TEST COMPOUND: SAMPLE#5 DBA-FGD SOLIDS (AQUEOUS LEACHATE)
B. SOLVENT: D.H2O
C. TEST INITIATION DATES: 01/06/82
D. TEST COMPLETION DATE: 01/11/82
E. S-9 LOT#: REG053
NOTE: CONCENTRATIONS ARE GIVEN IN MICROLITERS PER PLATE

TEST		SPECIES	TISSUE	REVERTANTS PER PLATE TA-1535 1	TA-1535 2	TA-1535 3	TA-1537 1	TA-1537 2	TA-1537 3	TA-98 1	TA-98 2	TA-98 3	TA-100 1	TA-100 2	TA-100 3
NONACTIVATION															
SOLVENT CONTROL		---	---	11	17		8	9		27	26		138	167	
POSITIVE CONTROL**		---	---	1227	1243		616	697		907	923		1785	1930	
TEST COMPOUND															
10.00	UL	---	---	15	10		10	17		20	20		103	96	
50.00	UL	---	---	21	13		13	12		19	16		105	132	
100.00	UL	---	---	18	15		10	5		19	18		122	129	
200.00	UL	---	---	17	13		9	7		20	25		129	138	
ACTIVATION															
SOLVENT CONTROL		RAT	LIVER	12	17		9	7		37	32		158	144	
POSITIVE CONTROL***		RAT	LIVER	406	422		478	378		2291	2352		2769	2958	
TEST COMPOUND															
10.00	UL	RAT	LIVER	17	14		9	10		21	24		103	107	
50.00	UL	RAT	LIVER	14	11		8	10		16	17		120	126	
100.00	UL	RAT	LIVER	10	15		10	11		26	19		141	157	
200.00	UL	RAT	LIVER	10	14		13	12		27	33		145	124	

**

TA-1535	SODIUM AZIDE	10 UG/PLATE
TA-1537	9-AMINOACRIDINE	50 UG/PLATE
TA-98	2-NITROFLUORENE	10 UG/PLATE
TA-100	SODIUM AZIDE	10 UG/PLATE
SOLVENT	200 UL/PLATE	

***

TA-1535	2-ANTHRAMINE	2.5 UG/PLATE
TA-1537	2-ANTHRAMINE	2.5 UG/PLATE
TA-98	2-ANTHRAMINE	2.5 UG/PLATE
TA-100	2-ANTHRAMINE	2.5 UG/PLATE

VII. ASSAY ACCEPTANCE AND EVALUATION CRITERIA

Statistical methods are not currently used, and evaluation is based on the criteria included in this protocol.

Plate test data consists of direct revertant colony counts obtained from a set of selective agar plates seeded with populations of mutant cells suspended in a semisolid overlay. Because the test material and the cells are incubated in the overlay for approximately 2 days and a few cell divisions occur during the incubation period, the test is semiquantitative in nature. Although these features of the assay reduce the quantitation of results, they provide certain advantages not contained in a quantitative suspension test:

- The small number of cell divisions permits potential mutagens to act on replication DNA, which is often more sensitive than nonreplicating DNA.

- The combined incubation of the test article and the cells in the overlay permits constant exposure of the indicator cells for approximately 2 days.

A. Surviving Populations

Plate test procedures do not permit exact quantitation of the number of cells surviving chemical treatment. At low concentrations of the test material, the surviving population on the treatment plates is essentially the same as that on the negative control plate. At high concentrations, the surviving population is usually reduced by some fraction. Our protocol will normally employ several doses ranging over two or three log concentrations, the highest of these doses being selected to show slight toxicity as determined by subjective criteria.

B. Dose-Response Phenomena

The demonstration of dose-related increased in mutant counts is an important criterion in establishing metagenicity. A factor that might modify dose-response results for a mutagen would be the selection of doses that are too low (usually mutagenicity and toxicity are related). If the highest dose is far lower than a toxic concentration, no increases may be observed over the dose range selected. Conversely, if the lowest dose employed is highly cytotoxic, the test material may kill any mutants that are induced, and the test material will not appear to be mutagenic.

C. Control Tests

Positive and negative control assays were conducted with each experiment and consisted of direct-acting mutagens for nonactivation assays and mutagens that require metabolic biotransformation in activation assays. Negative controls consisted of the test material solvent in the overlay agar together with the other essential components. The negative control plate for each strain gave a reference point to which the test data was compared. The positive control assay was conducted to demonstrate that the test systems were functional with known mutagens.

The following normal range of revertants for solvent controls are generally considered acceptable.

TA-1535:	8-30
TA-1537:	4-30
TA-98:	20-75
TA-100:	80-250

D. Evaluation Criteria for Ames Assay

Because the procedures to be used to evaluate the mutagenicity of the test material are semiquantitative, the criteria to be used to determine

positive effects are inherently subjective and are based primarily on a historical data base. Most data sets will be evaluated using the following criteria.

1. Strains TA-1535 and TA-1537

If the solvent control value is within the normal range, a test material that produces a positive dose response over three concentrations with the highest increase equal to three times the solvent control value will be considered to be mutagenic.

2. Strains TA-98 and TA-100

If the solvent control value is within the normal range, a test material that produces a positive dose response over three concentrations with the highest increase equal to twice the solvent control value for TA-98 and TA-100 will be considered to be mutagenic.

3. Pattern

Because TA-1535 and TA-100 are both derived from the same parental strain (G-46), to some extent there is a built-in redundancy in the microbial assay. In general, the two strains of a set respond to the same mutagen and such a pattern is sought. Generally, if a strain responds to a mutagen in nonactivation tests, it will do so in activation tests.

4. Reproducibility

If a test material produces a response in a single test that cannot be reproduced in additional runs, the initial positive test data lose significance.

The preceding criteria are not absolute, and other extenuating factors may enter into a final evaluation decision. However, these criteria will be applied to the majority of situations and are presented to aid those individuals not familar with this procedure. As the data base is increased, the criteria for evaluation can be more firmly established.

E. Relation Between Mutagenicity and Carcinogenicity

It must be emphasized that the Ames *Salmonella*/Microsome Plate Assay is not a definitive test for chemical carcinogens. It is recognized, however, that correlative and functional relations have been demonstrated between these two endpoints. The results of comparative tests on 300 chemicals by McCann *et al.*[4] show an extremely good correlation between results of microbial mutagenesis tests and *in vivo* rodent carcinogenesis assays.

All evaluations and interpretation of the data to be presented in the final report will be based only on the demonstration, or lack, of mutagenic activity.

F. Criteria for Ranking Samples in the Ames Assay

The goal of EPA Level 1 Ames testing is to rank source streams by relative degree of genetic toxicity (mutagenicity). Samples are first identified as mutagenic or nonmutagenic by the criteria in Section D above and then ranked using the mutagenicity categories presented in the table below. The lowest concentration giving a positive response in any strain, with or without metabolic activation, is identified as the minimum effective concentration (MEC) for that sample. The mutagenicity of the sample is evaluated as high (H), moderate (M), low (L), or nondetectable (ND) according to the evaluation criteria developed in the Level 1 manual[1] and summarized below. Samples with no detectable activity at the maximum applicable dose (MAD) are ranked nondetectable (ND).

Another evaluation scheme is proposed for extracts obtained from SASS train gas volumes. The proportion of the total gas volume corresponding to the volume of extract used in the bioassay is calculated and expressed as liters per plate. A criterion of 5000 L/plate is set as the limit for nondetectable toxicity. The subsequent toxicity ranges are defined by 10-fold dilution steps to conform to standard procedure. Evaluation criteria based on equivalent gas volumes are tentative and under evaluation.

Ames Assay Mutagenicity Ranking Criteria[1]

Mutagenic Activity	Solids (MEC in μg/plate)	Liquids[a] (MEC in μl/plate)	Equivalent Gas Volumes (MEC in liters/plate)
High (H)	<50	<2	<50
Moderate (M)	50-500	2-20	50-500
Low (L)	500-5000	20-200	500-5000
Not Detectable (ND)	>5000	>200	>5000

[a]Concentration of organic extracts is based upon organic content (μg organics per plate) and not volume (μl extract per plate) of sample tested.

VIII. REFERENCES

1. Brusick, D.J., et al.: IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests. EPA-600/8-81-024, Litton Bionetics, Inc., Kensington, MD, October, 1981, 177 pp.

2. Brusick, D.J.: Level 1 Bioassay Assessment and Data Formatting. EPA-600/7-80-079, Litton Bionetics Inc., Kensington, MD, April 1980, 100 pp.

3. Brusick, D.J. and Young, R.R.: Level 1 Bioassay Sensitivity. EPA-600/7-81-135, Litton Bionetics, Inc., Kensington, MD, August 1981, 52 pp.

4. McCann, J., Choi, E., Yamasaki, E. and Ames, B.N.: Detection of carcinogens as mutagens in the Salmonella/microsome test: Assay of 300 chemicals. Proc. Nat. Acad. Sci., USA 72:5135-5139, 1975.

5. Ames, B.N., Gurney, E.G., Miller, J.A. and Bartsch, H.: Carcinogens as frameshift mutagens: Metabolites and derivatives of 2-acetylaminofluorene and other aromatic amine carcinogens. Proc. Nat. Acad. Sci., USA 69:3128-3132, 1972.

6. Ames, B.N., Lee, F.D., and Durston, W.E.: An improved bacterial test system for the detection and classification of mutagens and carcinogens. Proc. Nat. Acad. Sci., USA 70:782-786, 1973.

7. Ames, B.N., Durston, W.E., Yamasaki, E. and Lee, F.D.: Carcinogens are mutagens: A simple test system combining liver homogenates for activation and bacteria for detection. Proc. Nat. Acad. Sci., USA 70:2281-2285, 1973.

8. McCann, J., Springarn, N.E., Kobori, J. and Ames, B.N.: Detection of carcinogens as mutagens: Bacterial tester strains with R factor plasmids. Proc. Nat. Acad. Sci. USA 72:979-983, 1975.

9. Ames, B.N., McCann, J. and Yamasaki, E.: Methods for detecting carcinogens and mutagens with the Salmonella/mammalian-microsome mutagenicity test. Mutation Res., 31:347-364, 1975.

10. Vogel, H.J. and Bonner, D.M.: Acetylornithinase of E. coli partial purification and some properties. J. Biol. Chem., 218:97-106, 1966.

GENETICS ASSAY NOS. 6045-6048
LBI SAFETY NOS. 7383-7386

APPENDIX F

CYTOTOXIC EVALUATION OF SOLID FGD SLUDGE SAMPLES IN THE EPA LEVEL 1 RODENT CELL (CHO) CLONAL TOXICITY ASSAY

FINAL REPORT

SUBMITTED TO:

RADIAN CORPORATION
8501 MO-PAC BOULEVARD
P.O. BOX 9948
AUSTIN, TEXAS 78766-0948

SUBMITTED BY:

LITTON BIONETICS, INC.
5516 NICHOLSON LANE
KENSINGTON, MARYLAND 20895

LBI PROJECT NO. 20993

REPORT DATE: JANUARY 1982

PREFACE

This assay conforms to the standard EPA Level 1 procedure for the Chinese hamster ovary cell (CHO) clonal toxicity assay as described in "IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests"[1]. The data were evaluated and formatted as recommended in "Level 1 Biological Testing Assessment and Data Formatting"[2].

The CHO clonal toxicity assay has been shown to be a sensitive method for detecting cytotoxic activity for a variety of chemicals representing various chemical classes [3]. This assay is one of several recommended by EPA to identify, categorize and rank the pollutant potential of influent and effluent streams from industrial and energy-producing processes. This assay has been well validated with a wide range of positive and negative control chemicals and complex environmental samples.

All procedures and documents pertaining to the receipt, storage, preparation, testing and evaluation of the test material shall conform to Litton Bionetics, Inc. standard operating procedures and the Good Laboratory Practices Regulations of 1979. Deviations from standard procedure shall be fully documented and noted in the report.

All test and control results in this report are supported by fully documented raw data which are permanently maintained in the files of the Department of Molecular Toxicology or in the archives of Litton Bionetics, Inc., 5516 Nicholson Lane, Kensington, Maryland 20895. Copies of raw data will be supplied to the sponsor upon request.

TABLE OF CONTENTS

		Page No.
PREFACE		i
I.	ASSAY SUMMARY	1
II.	OBJECTIVE	2
III.	TEST MATERIAL	3
	A. Description	3
	B. Handling and Preparation	3
IV.	MATERIALS	5
	A. Indicator Cells	5
	B. Media	5
	C. Controls	6
V.	EXPERIMENTAL DESIGN	7
	A. Dose Selection	7
	B. Clonal Toxicity Assay	7
VI.	RESULTS	9
	A. Interpretation	9
	1. Sample #1, Solid FGD Sludge	10
	2. Sample #2, Solid FGD Sludge	10
	3. Sample #4, Solid FGD Sludge	10
	4. Sample #5, DBA-FGD Sludge	10
	B. Tables and Figures	11
VII.	ASSAY ACCEPTANCE CRITERIA	28
VIII.	ASSAY EVALUATION CRITERIA	29
IX.	REFERENCES	30

I. SUMMARY

The four FGD sludge samples (Nos. 1, 2, 4 and 5) supplied by Radian Corporation were tested and evaluated for their cytotoxicities in the EPA Level 1 Chinese hamster ovary (CHO) cell clonal toxicity assay. The samples were tested directly in their solid forms and as aqueous leachates.

The solid forms of the four samples were all found to have nondetectable toxicity; that is, the EC_{50} values were greater than 1000 μg of sample per ml of culture medium. The aqueous leachates of samples #1, #2 and #4 were also ranked as having nondetectable toxicity based upon EC_{50} values greater than 600 μl of leachate per ml of culture medium. The aqueous leachate of sample #5 was weakly toxic to the cells. An EC_{50} of 545 μl per ml was observed for this leachate which placed the sample in the low toxicity category but very close to the low/nondetectable boundary of 600 μl per ml. Therefore, the sample was ranked as having low/nondetectable (L/ND) borderline toxicity.

Submitted by:

Study Director

Brian C Myhr 1/29/82

Brian Myhr, Ph.D. Date
Associate Director,
Department of Molecular
Toxicology

Reviewed by:

David J. Brusick 2/1/82

David J. Brusick, Ph.D. Date
Director,
Department of Molecular
Toxicology

II. OBJECTIVE

The objective of this study was to determine and rank the cytotoxicities of four solid FGD sludge samples to cultured Chinese hamster cells (CHO-K1 cell line). To provide a more complete assessment of the toxicities of the FGD sludge samples, CHO clonal toxicity tests were performed on the test materials as they were received (solid form) and on aqueous leachates of the test materials. The measure of cytotoxicity was the reduction in colony-forming ability of CHO-K1 cells after a 24-hour exposure to the test material. After a period of recovery and growth, the number of colonies that developed in the treated cultures was compared to the colony number in unexposed vehicle control cultures. The concentration of test material that reduced the colony number by 50 percent was estimated graphically and referred to as the EC_{50} value. Standard EPA Level 1 toxicity evaluation criteria for the CHO clonal toxicity assay were used to rank the toxicity potential of each test material.

III. TEST MATERIAL

A. Description

Four samples were supplied by Radian Corporation, Austin, Texas. The samples were assigned LBI safety numbers and LBI assay numbers upon receipt. The Radian code numbers, sample identification, LBI safety numbers and LBI assay numbers are as follows:

Radian Corp. Code	Sample Identification	LBI Safety No.	LBI Assay No.
Sample #1	Solid FGD Sludge (natural oxidation with flyash and soil)	7383	6045
Sample #2	Solid FGD Sludge (natural oxidation with flyash, soil and adipic acid)	7384	6046
Sample #4	Solid FGD Sludge (forced oxidation with flyash, soil and adipic acid)	7385	6047
Sample #5	DBA-FGD Solids (with flyash, soil and dibasic acid)	7386	6048

Sample #1 was received as a brown/gray granular particulate with white flakes. Sample #2 was a fine, dark brown/gray powder. Sample #4 consisted of sand-like particles of a light tan color. Sample #5 was a coarse, variable-sized particulate of black and gray color.

No information on sampling parameters was provided.

B. Handling and Preparation

The test materials were received at LBI on November 30, 1981. The samples were individually packed in zip-lock plastic bags and placed inside a cardboard carton. The samples were received intact and were stored at +4°C in the dark until used.

The samples were tested in the CHO clonal toxicity assay, both in the original solid forms and as aqueous leachates. The solid forms of the samples were tested as suspensions in F12 culture medium. The maximum concentration of 1000 μg/ml was prepared by suspending test material directly in F12 culture medium. The suspensions were vortexed and sonicated to prepare a uniform suspension of test material. The suspensions were then placed on a roller drum at 37°C for about 5 hours to leach the test materials. Lower concentrations were prepared by making dilutions with F12 culture medium.

Aqueous leachates of the samples were prepared by shaking 30 gm of each sample with 120 ml of sterile deionized water at 200 rpm for 48 hours. The suspensions were allowed to settled, and the supernatants were decanted into 50 ml conical centrifuge tubes and centrifuged for 20 minutes at 850 x g. The leachates were then filtered through 0.45 μm Nalgene filters and stored in sterile tissue culture flasks at +4°C in the dark.

A total volume of 18 ml of each test material leachate was used in testing. The maximum concentration of 600 μl/ml was obtained by diluting 18 ml of each leachate with 10X F10 medium and other medium components to achieve a final 1X concentration of F10 medium. The lower concentrations were prepared by serial dilution with 1X F10 growth medium.

IV. MATERIALS

A. Indicator Cells

The indicator cells for these assays were Chinese hamster CHO-K1 cells (ATCC No. CCL 61) obtained from Flow Laboratories, Inc., Rockville, MD. This cell type was derived from ovarian tissue and has spontaneously transformed to a stable, hypodiploid line of rounded, fibroblastic cells with unlimited growth potential. Monolayer cultures have a fast doubling time of 11 to 14 hours, and untreated cells can normally be cloned with an efficiency of 80 percent or greater. Laboratory stocks were maintained by routine serial subpassage. Cells were cultivated in Ham's F-12 nutrient medium at 37°C in an atmosphere of 5 percent CO_2 and saturated humidity. Stocks were continually observed macroscopically and microscopically for possible microbial contamination. Laboratory cultures were periodically checked by culturing and staining methods for the absence of mycoplasma contamination. Laboratory cultures were discarded every three months and new cultures started from mycoplasma-free, long-term frozen cultures.

B. Media

The CHO-K1 cell line has an absolute requirement for proline and therefore must be maintained in culture medium containing sufficient amounts of this amino acid. Ham's F12 medium, which contains 3×10^{-4} M L-proline was used, supplemented with 10 percent fetal bovine serum, 2mM L-glutamine, 100 units/ml of penicillin, 100 μg/ml of streptomycin, and 0.9 μl/ml of amphotericin B. A 10X formulation of Ham's F10 is available commercially and was used for testing the aqueous leachate of the test samples in order to avoid the dilution of medium components. This medium contains 1×10^{-4} M L-proline and was supplemented in the same manner as F12, except that kanamycin at 40 μg/ml was included for additional protection against bacterial contamination. Both media formulations support the growth and cloning of CHO cells equally well.

C. Controls

The negative control for all assays consisted of three untreated cultures in F12 medium carried through the same experimental time period as the treated cells. The vehicle control for assays testing the aqueous leachates consisted of three cultures exposed to 1X F10 culture medium for the treatment period, then returned to F12 medium for colony development. The average number of colonies in the negative control established the cloning efficiency of the CHO cells used in the assays and the reference point for determining the effects of different concentrations of the solid test materials on cell survival. In the trials with the aqueous leachates, the F10 vehicle control provided the reference point for calculating the relative survival to the test concentrations.

V. EXPERIMENTAL DESIGN

A. Dose Selection

Unless the approximate toxicity is already known, or the sample size is limiting, the following dose ranges are usually tested for different sample forms. Aqueous samples, suspensions, or slurries are tested from 600 µl/ml to 10 µl/ml, usually in six dose steps. Eight doses are often used when the amount of test sample is limited to provide a more precise description of toxicity in the event of sharp dose-response curves. Dry, particulate material is dissolved or suspended in culture medium and tested at ten dose levels from 1000 µg/ml to 1 µg/ml. Samples that are solvent-exchanged into DMSO are tested from 20 µl/ml (2 percent DMSO in growth medium) to 0.2 µl/ml, in six dose steps. A second dose study is performed with an adjusted dose range if the EC50 was not located properly in the initial test. However, EC50 values greater than 1000 µg/ml for particulate material, 600 µl/ml for aqueous samples, or 20 µl/ml for organic solutions will not be determined.

In this work the test materials were tested both as solids and as aqueous leachates. The concentrations used for the solid forms started with the maximum applicable dose (MAD) of 1000 µg/ml and included 9 other doses from 600 µg/ml to 1 µg/ml. The aqueous leachates of the test samples were tested at six doses ranging from the MAD of 600 µl/ml down to 10 µl/ml.

B. Clonal Toxicity Assay

Cells from monolayer stock cultures in logarithmic growth phase were trypsinized with 0.1 percent trypsin plus 0.01 percent versene for 4 minutes, and the density of the resulting cell suspension was determined by hemocytometer. A number of 60-mm culture dishes were then seeded with 200 cells and 4 ml of culture medium per dish. The cultures were incubated for approximately 6 hours at 37°C in a humidified atmosphere containing 5 percent CO_2 to allow attachment of the cells. The 6-hour

attachment period was used in order to avoid cell division and the subsequent formation of two-cell colonies prior to treatment.

The medium was aspirated from the cultures and 4 ml of control medium or medium containing the test material was applied. Three cultures were exposed to each test concentration. After an exposure time of 24 hours at 37°C, the medium was removed by aspiration and each culture washed two times with approximately 4 ml aliquots of Dulbecco's phosphate buffered saline (pre-warmed to 37°C). Fresh culture medium (5 ml) was placed in each dish, and incubation at 37°C was continued for an additional 6 days to allow colony development.

If the test material caused a color change in the culture medium, the pH of the medium containing the high dose would be determined at the time of treatment. The pH at the lowest dose that results in a slight color change would also be recorded. At the end of the treatment period, the pH values of the discarded media from the two described treatments would be recorded again. No sample-related pH changes were noted in any of the treatments.

After the incubation period, the medium was drained from the cultures, and the surviving colonies were fixed with 100 percent ethanol and stained with Giemsa. Colonies were counted by eye; tiny colonies of approximately 50 cells or less were arbitrarily excluded from the counts.

VI. RESULTS

A. Interpretation

The results of the Chinese hamster ovary (CHO) clonal toxicity assays are presented in Tables 1 through 8. The calculated relative survival values were obtained by comparing the average number of colonies per dish for each of the assayed concentrations to the appropriate control value. The relative survival values were then plotted as functions of the applied concentration of test material per ml of culture medium in Figures 1 through 8. Curves were fitted to the data points by eye in order to determine the EC_{50} value for each sample and to rank each sample according to EPA Level 1 evaluation criteria.

1. Sample #1, Solid FGD Sludge

The test material in both the solid and aqueous leachate forms caused only small reductions in the colony forming ability of cultured CHO cells. The solid form of the sample produced a gradual reduction in cell survival over the range of concentrations tested (1 μg to 1000 μg/ml) and reduced the survival to about 60 percent at the maximum applicable dose (MAD) of 1000 μg/ml (Figure 1). Since the EC_{50} value was clearly greater than 1000 μg/ml, the sample was ranked as having nondetectable (ND) toxicity.

The aqueous leachate of sample #1 caused no toxicity between 10 μl and 100 μl/ml, but a gradually increasing toxicity was observed between 100 μl and 600 μl/ml (Figure 2). While some toxicity was observed in the low toxicity range (60 μl to 600 μl/ml), no concentration reduced the relative survival below 76 percent. The EC_{50} was greater than 600 μl/ml and the test material was ranked as having nondetectable (ND) toxicity.

2. Sample #2, Solid FGD Sludge

The toxic response of CHO cells to both the solid and aqueous leachate forms of sample #2 was very similar to that observed for sample #1. Gradually increasing toxicity was caused by the solid form of the sample (Figure 3). Maximum toxicity was observed at the MAD of 1000 μg/ml and the survival was about 65 percent. The sample was therefore ranked as having nondetectable (ND) toxicity.

The aqueous leachate of sample #2 gave negligible toxicity below 100 μl/ml, and the toxicity increased only slightly as the concentration increased from 100 μl to 600 μl/ml (Figure 4). The survival at 600 μl/ml was about 81 percent; so the sample was ranked as having nondetectable (ND) toxicity.

3. Sample #4, Solid FGD Sludge

The solid form of sample #4 produced no increase in toxicity between 1 μg and 300 g/ml. A very slight increase in toxicity was noted above 300 μg/ml, causing a reduction in survival to 85 percent at the MAD of 1000 μg/ml (Figure 5). Therefore, the EC_{50} was greater than 1000 μg/ml and the sample was ranked as having nondetectable (ND) toxicity.

The aqueous leachate of the sample caused a gradually increasing toxicity over the range of doses tested (10 μl to 600 μl/ml) (Figure 6). The relative survival did not approach 50 percent and reached a minimum of 69.5 percent at the MAD of 600 μl/ml. The sample was ranked as having nondetectable (ND) toxicity.

4. Sample #5, DBA-FGD Solids

Gradually increasing toxicity was observed for the solid form of sample #5 between 1 μg and 300 μg/ml. As occurred for the solid form of sample #4, an increase in toxicity was obtained at concentrations above

300 μg/ml. The relative survival did not fall below 66 percent (1000 μg/ml), so the EC_{50} was greater than 1000 μg/ml (Figure 7). Thus, the sample was ranked as having nondetectable (ND) toxicity.

The assay on the aqueous form of sample #5 was the only test in this series where an EC_{50} value was observed. The sample had negligible toxicity between 10 μl and 100 μl/ml, but the toxicity increased steadily from 100 μl to 600 μl/ml and reached a maximum corresponding to 45.9 percent relative survival at 600 μl/ml (Figure 8). The EC_{50} was estimated to be 545 μl/ml, a value in the low toxicity range but one which closely approached the low/nondetectable boundary of 600 μl/ml. Because of normal experimental variation, repeat trials could be expected to produce EC_{50} values at, or somewhat above, the low/nondetectable borderline. For this reason, the aqueous form of sample #5 was ranked as having low/nondetectable (L/ND) borderline toxicity.

The cells used for the eight assays were in logarithmic growth phase and were at least 97 percent viable (average value of 99.4±0.5 percent). Greater than 70 percent of the seeded cells formed colonies in the negative controls of each of the eight assays (77.6±6.7 percent). Colony growth was normal and well distributed on the culture dishes in all trials. The combined results were considered to achieve assay acceptance criteria and provided confidence in the assumption that the recorded data represented typical responses to the test materials.

B. Tables and Figures

This report is based on the data provided in Tables 1 through 8 and Figures 1 through 8.

TABLE 1

CLONAL CYTOTOXICITY ASSAY

SAMPLE IDENTITY: SAMPLE # 1, SOLID FGD SLUDGE (SOLID)

DESCRIPTION OF SAMPLE: BROWN/GRAY GRANULAR PARTICLES WITH FLAKES

LBI ASSAY NO. 6045 SOLID

DATE RECEIVED: NOVEMBER 30 1981

TEST DATE: DECEMBER 7, 1981

VEHICLE: F12 MEDIUM

CELL TYPE: CHO-K1

CELLS SEEDED PER DISH: 200

EC50 VALUE: > 1000 MICROGRAMS/ML

TOXICITY CLASSIFICATION: NONDETECTABLE (ND)

PH ALTERATIONS: NONE

COMMENTS ON TREATMENT:

COLONY COUNTS

SAMPLE	APPLIED CONCENTRATION UG/ML	DISH #1	DISH #2	DISH #3	AVERAGE COUNT	RELATIVE SURVIVAL* (PERCENT)	CLONING EFFICIENCY (PERCENT)
NC		140	141	142	141.0		70.5
TEST	1	123	128	137	129.3	91.7	
TEST	3	109	108	121	112.7	79.9	
TEST	6	110	107	104	107.0	75.9	
TEST	10	107	113	116	112.0	79.4	
TEST	30	110	111	119	113.3	80.4	
TEST	60	85	105	110	100.0	70.9	
TEST	100	115	107	92	104.7	74.3	
TEST	300	87	105	93	95.0	67.4	
TEST	600	93	95	99	95.7	67.9	
TEST	1000	90	84	81	85.0	60.3	

NC = NEGATIVE CONTROL, F12 MEDIUM

*RELATIVE TO NEGATIVE CONTROL

TABLE 2

CLONAL CYTOTOXICITY ASSAY

SAMPLE IDENTITY: SAMPLE #1, SOLID FGD SLUDGE (LEACHATE)

DESCRIPTION OF SAMPLE: CLEAR LIQUID

LBI ASSAY NO. 6045 LEACHATE

DATE RECEIVED: NOVEMBER 30, 1981

TEST DATE: DECEMBER 12,1981

VEHICLE: F10 MEDIUM

CELL TYPE: CHO-K1

CELLS SEEDED PER DISH: 200

EC50 VALUE: > 600 MICROLITERS/ML

TOXICITY CLASSIFICATION: NONDETECTABLE (ND)

PH ALTERATIONS: NONE

COMMENTS ON TREATMENT:

COLONY COUNTS

SAMPLE	APPLIED CONCENTRATION UL/ML	DISH #1	DISH #2	DISH #3	AVERAGE COUNT	RELATIVE SURVIVAL* (PERCENT)	CLONING EFFICIENCY (PERCENT)
NC	---	172	173	180	175.0		87.5
VC	---	179	183	186	182.7	100.0	91.4
TEST	10	173	180	174	175.7	96.2	
TEST	30	169	167	174	170.0	93.0	
TEST	60	164	170	179	171.0	93.6	
TEST	100	173	175	174	174.0	95.2	
TEST	300	150	151	151	150.7	82.5	
TEST	600	138	142	140	140.0	76.6	

NC = NEGATIVE CONTROL, F12 MEDIUM
VC = VEHICLE CONTROL, F10 MEDIUM

*RELATIVE TO VC FOR ALL TREATMENTS

TABLE 3

CLONAL CYTOTOXICITY ASSAY

SAMPLE IDENTITY: SAMPLE # 2, SOLID FCC SLUDGE (SOLID)

DESCRIPTION OF SAMPLE: FINE, DARK BROWN/ GRAY POWDER

LEI ASSAY NO. 6046 SOLID

DATE RECEIVED: NOVEMBER 30, 1981

TEST DATE: DECEMBER 7, 1981

VEHICLE: F12 MEDIUM

CELL TYPE: CHO-K1

CELLS SEEDED PER DISH: 200

EC50 VALUE: > 1000 MICROGRAMS/ML

TOXICITY CLASSIFICATION: NONDETECTABLE (ND)

PH ALTERATIONS: NONE

COMMENTS ON TREATMENT:

COLONY COUNTS

SAMPLE	APPLIED CONCENTRATION UG/ML	DISH #1	DISH #2	DISH #3	AVERAGE COUNT	RELATIVE SURVIVAL* (PERCENT)	CLONING EFFICIENCY (PERCENT)
NC	---	135	149	145	143.0		71.5
TEST	1	120	129	135	128.0	89.5	
TEST	3	105	109	110	108.0	75.5	
TEST	6	100	111	108	106.3	74.3	
TEST	10	106	114	114	111.3	77.8	
TEST	30	102	94	111	102.3	71.5	
TEST	60	100	108	107	105.0	73.4	
TEST	100	106	112	96	104.7	73.2	
TEST	300	96	101	102	99.7	69.7	
TEST	600	95	92	94	93.7	65.5	
TEST	1000	91	94	97	94.0	65.7	

NC = NEGATIVE CONTROL, F12 MEDIUM

*RELATIVE TO NEGATIVE CONTROL

TABLE 4

CLONAL CYTOTOXICITY ASSAY

SAMPLE IDENTITY: SAMPLE # 2, SOLID FGD SLUDGE (LEACHATE)

DESCRIPTION OF SAMPLE: CLEAR LIQUID

LBI ASSAY NO. 6046 LEACHATE

DATE RECEIVED: NOVEMBER 30, 1981

TEST DATE: DECEMBER 17, 1981

VEHICLE: F10 MEDIUM

CELL TYPE: CHO-K1

CELLS SEEDED PER DISH: 200

EC50 VALUE: > 600 MICROLITERS/ML

TOXICITY CLASSIFICATION: NONDETECTABLE (ND)

PH ALTERATIONS: NONE

COMMENTS ON TREATMENT:

COLONY COUNTS

SAMPLE	APPLIED CONCENTRATION UL/ML	DISH #1	DISH #2	DISH #3	AVERAGE COUNT	RELATIVE SURVIVAL* (PERCENT)	CLONING EFFICIENCY (PERCENT)
NC	---	172	173	180	175.0		87.5
VC	---	179	183	186	182.7	100.0	91.4
TEST	10	153	166	162	160.3	87.7	
TEST	30	162	169	166	165.7	90.7	
TEST	60	164	170	169	167.7	91.8	
TEST	100	160	167	168	165.0	90.3	
TEST	300	154	148	152	151.3	82.8	
TEST	600	150	153	144	145.0	81.6	

NC = NEGATIVE CONTROL, F12 MEDIUM
VC = VEHICLE CONTROL, F10 MEDIUM

*RELATIVE TO VC FOR ALL TREATMENTS

TABLE 5

CLONAL CYTOTOXICITY ASSAY

SAMPLE IDENTITY: SAMPLE # 4, SOLID FCD SLUDGE (SOLID)

DESCRIPTION OF SAMPLE: LIGHT TAN, SAND-LIKE PARTICLES

LBI ASSAY NO. 6047 SOLID

DATE RECEIVED: NOVEMBER 30, 1981

TEST DATE: DECEMBER 10, 1981

VEHICLE: F12 MEDIUM

CELL TYPE: CHO-K1

CELLS SEEDED PER DISH: 200

FC50 VALUE: > 1000 MICROGRAMS/ML

TOXICITY CLASSIFICATION: NONDETECTABLE (ND)

PH ALTERATIONS: NONE

COMMENTS ON TREATMENT:

COLONY COUNTS

SAMPLE	APPLIED CONCENTRATION UG/ML	DISH #1	DISH #2	DISH #3	AVERAGE COUNT	RELATIVE SURVIVAL* (PERCENT)	CLONING EFFICIENCY (PERCENT)
NC	---	148	155	158	153.7		76.9
TEST	1	155	148	144	149.0	96.9	
TEST	3	136	147	143	142.0	92.4	
TEST	6	152	136	138	142.0	92.4	
TEST	10	147	135	149	143.7	93.5	
TEST	30	144	147	152	147.7	96.1	
TEST	60	148	138	153	146.3	95.2	
TEST	100	139	145	151	145.0	94.3	
TEST	300	147	143	150	146.7	95.4	
TEST	600	141	134	135	136.7	88.9	
TEST	1000	125	130	136	130.3	84.8	

NC = NEGATIVE CONTROL, F12 MEDIUM

*RELATIVE TO NEGATIVE CONTROL

TABLE 6

CLONAL CYTOTOXICITY ASSAY

SAMPLE IDENTITY: SAMPLE # 4, SCLIC FCC SLUDGE (LEACHATE)

DESCRIPTION OF SAMPLE: CLEAR LIQUID

LBI ASSAY NO. 6047 LEACHATE

DATE RECEIVED: NOVEMBER 30, 1981

TEST DATE: DECEMBER 21, 1981

VEHICLE: F10 MEDIUM

CELL TYPE: CHO-K1

CELLS SEEDED PER DISH: 200

EC50 VALUE: > 600 MICROLITERS/ML

TOXICITY CLASSIFICATION: NONDETECTABLE (ND)

PH ALTERATIONS: NONE

COMMENTS ON TREATMENT:

COLONY COUNTS

SAMPLE	APPLIED CONCENTRATION UL/ML	DISH #1	DISH #2	DISH #3	AVERAGE COUNT	RELATIVE SURVIVAL* (PERCENT)	CLONING EFFICIENCY (PERCENT)
NC	---	150	130	162	147.3		73.7
VC	---	149	148	143	146.7	100.0	73.4
TEST	10	123	127	139	129.7	88.4	
TEST	30	121	116	124	120.3	82.0	
TEST	60	121	108	117	115.3	78.6	
TEST	100	111	119	108	112.7	76.8	
TEST	300	103	107	106	105.3	71.8	
TEST	600	100	101	105	102.0	69.5	

NC = NEGATIVE CONTROL, F12 MEDIUM
VC = VEHICLE CONTROL, F10 MEDIUM

*RELATIVE TO VC FOR ALL TREATMENTS

TABLE 7

CLONAL CYTOTOXICITY ASSAY

SAMPLE IDENTITY: SAMPLE # 5, DEA-FED SOLIDS (SOLID)

DESCRIPTION OF SAMPLE: COARSE, VARIABLE-SIZED PARTICLES OF BLACK AND GRAY COLOR

LBI ASSAY NO. 6048 SOLID

DATE RECEIVED: NOVEMBER 30, 1981

TEST DATE: DECEMBER 10, 1981

VEHICLE: F12 MEDIUM

CELL TYPE: CHO-K1

CELLS SEEDED PER DISH: 200

EC50 VALUE: > 1000 MICROGRAMS/ML

TOXICITY CLASSIFICATION: NONDETECTABLE (ND)

PH ALTERATIONS: NONE

COMMENTS ON TREATMENT:

COLONY COUNTS

SAMPLE	APPLIED CONCENTRATION UG/ML	DISH #1	DISH #2	DISH #3	AVERAGE COUNT	RELATIVE SURVIVAL* (PERCENT)	CLONING EFFICIENCY (PERCENT)
NC	---	154	165	158	159.0		79.5
TEST	1	141	164	147	150.7	94.8	
TEST	3	131	148	142	140.3	88.2	
TEST	6	130	149	136	138.0	86.8	
TEST	10	147	151	140	146.0	91.8	
TEST	30	143	136	149	142.7	89.7	
TEST	60	122	145	130	132.3	83.2	
TEST	100	127	124	123	124.7	78.4	
TEST	300	130	140	128	132.7	83.5	
TEST	600	126	115	117	119.3	75.0	
TEST	1000	96	107	112	105.0	66.0	

NC = NEGATIVE CONTROL, F12 MEDIUM

*RELATIVE TO NEGATIVE CONTROL

TABLE 8

CLONAL CYTOTOXICITY ASSAY

SAMPLE IDENTITY: SAMPLE # 5, DEA-FCD SCLIDS (LEACHATE)

DESCRIPTION OF SAMPLE: CLEAR LIQUID

LBI ASSAY NO. 604B LEACHATE

DATE RECEIVED: NOVEMBER 30, 1981

TEST DATE: DECEMBER 21, 1981

VEHICLE: F10 MEDIUM

CELL TYPE: CHO-K1

CELLS SEEDED PER DISH: 200

EC50 VALUE: 545 MICROLITERS/ML

TOXICITY CLASSIFICATION: LOW (L)

PH ALTERATIONS: NONE

COMMENTS ON TREATMENT:

COLONY COUNTS

SAMPLE	APPLIED CONCENTRATION UL/ML	DISH #1	DISH #2	DISH #3	AVERAGE COUNT	RELATIVE SURVIVAL* (PERCENT)	CLONING EFFICIENCY (PERCENT)
NC	---	150	130	162	147.3		73.7
VC	---	149	148	143	146.7	100.0	73.4
TEST	10	130	131	139	133.3	90.9	
TEST	30	121	129	128	126.0	85.9	
TEST	60	135	127	126	129.3	88.1	
TEST	100	126	126	121	124.3	84.7	
TEST	300	107	83	111	100.3	68.4	
TEST	600	65	67	70	67.3	45.9	

NC = NEGATIVE CONTROL, F12 MEDIUM
VC = VEHICLE CONTROL, F10 MEDIUM

*RELATIVE TO VC FOR ALL TREATMENTS

FIGURE 1

RODENT CELL (CHO) CLONAL TOXICITY ASSAY

EC_{50} DETERMINATION

SAMPLE # 1, SOLID FGD SLUDGE

SOLID FORM

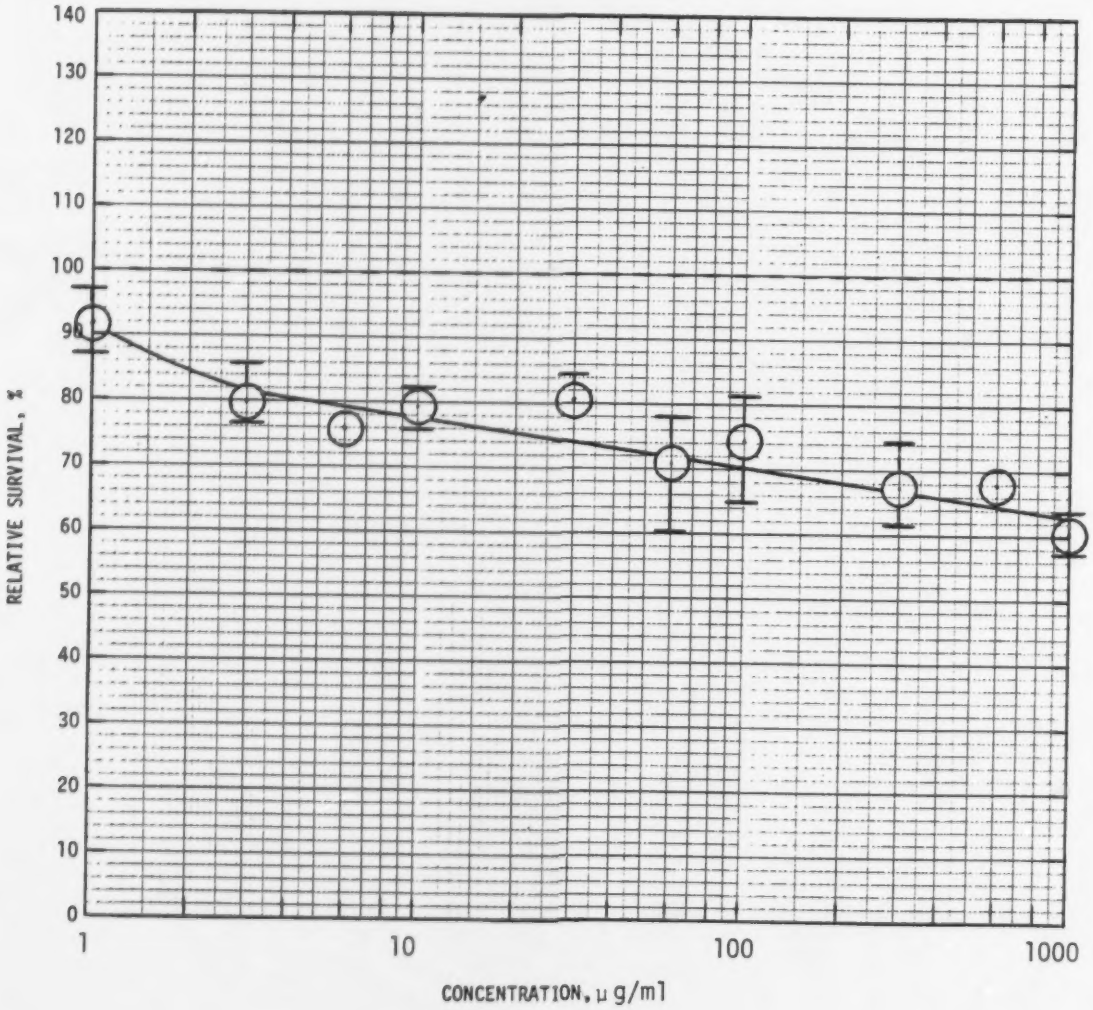


FIGURE 2

RODENT CELL (CHO) CLONAL TOXICITY ASSAY

EC_{50} DETERMINATION

SAMPLE # 1, SOLID FGD SLUDGE

AQUEOUS LEACHATE FORM

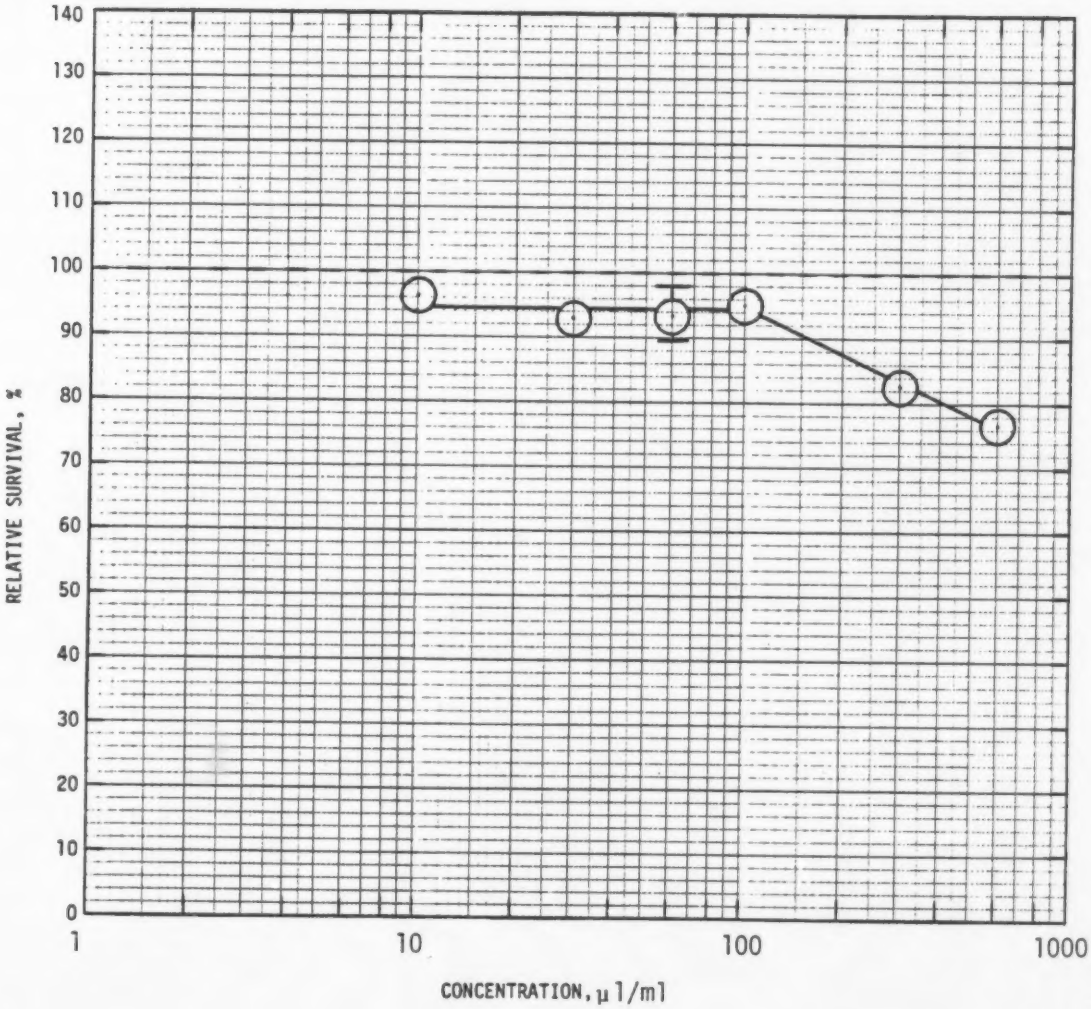


FIGURE 3

RODENT CELL (CHO) CLONAL TOXICITY ASSAY

EC_{50} DETERMINATION

SAMPLE # 2, SOLID FGD SLUDGE

SOLID FORM

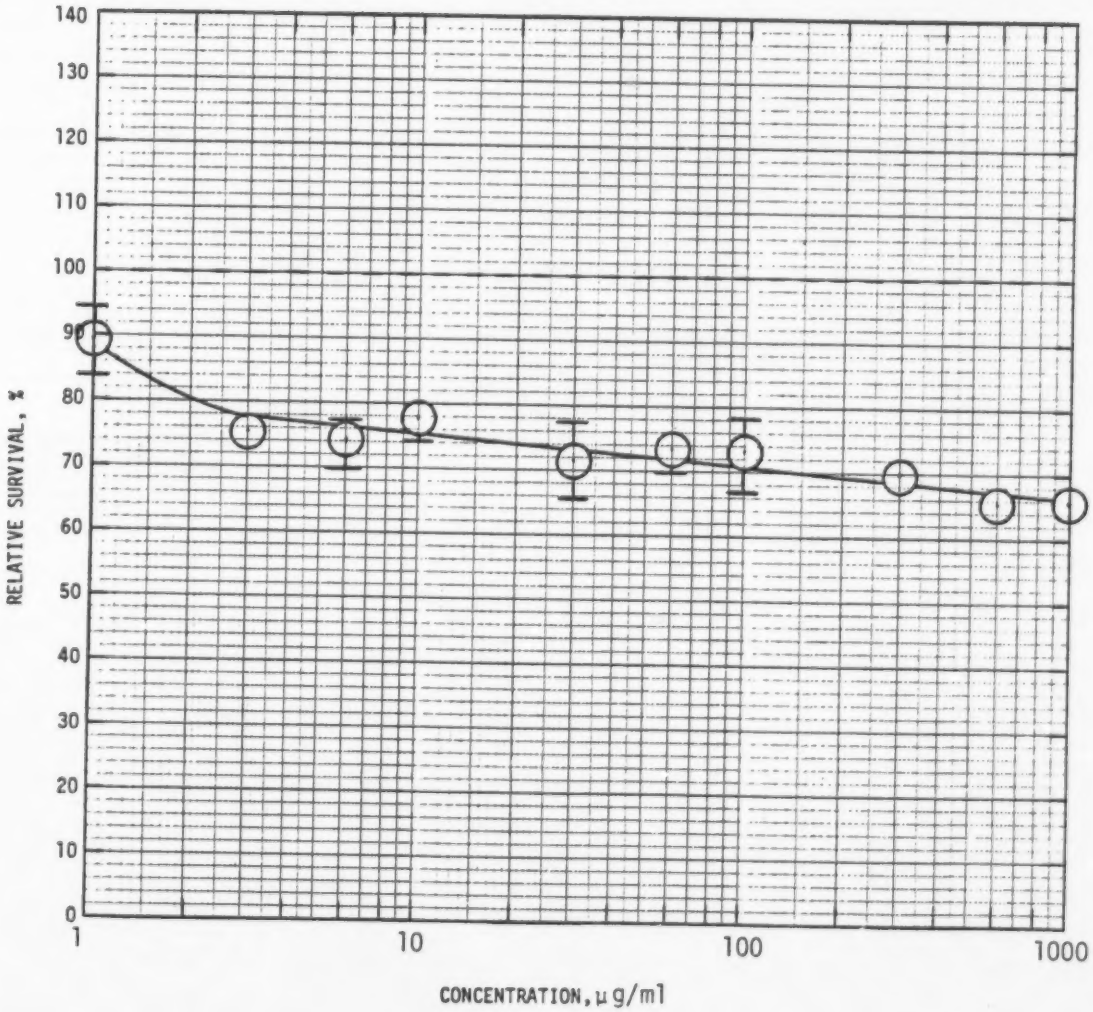


FIGURE 4

RODENT CELL (CHO) CLONAL TOXICITY ASSAY

EC_{50} DETERMINATION

SAMPLE # 2, SOLID FGD SLUDGE

AQUEOUS LEACHATE FORM

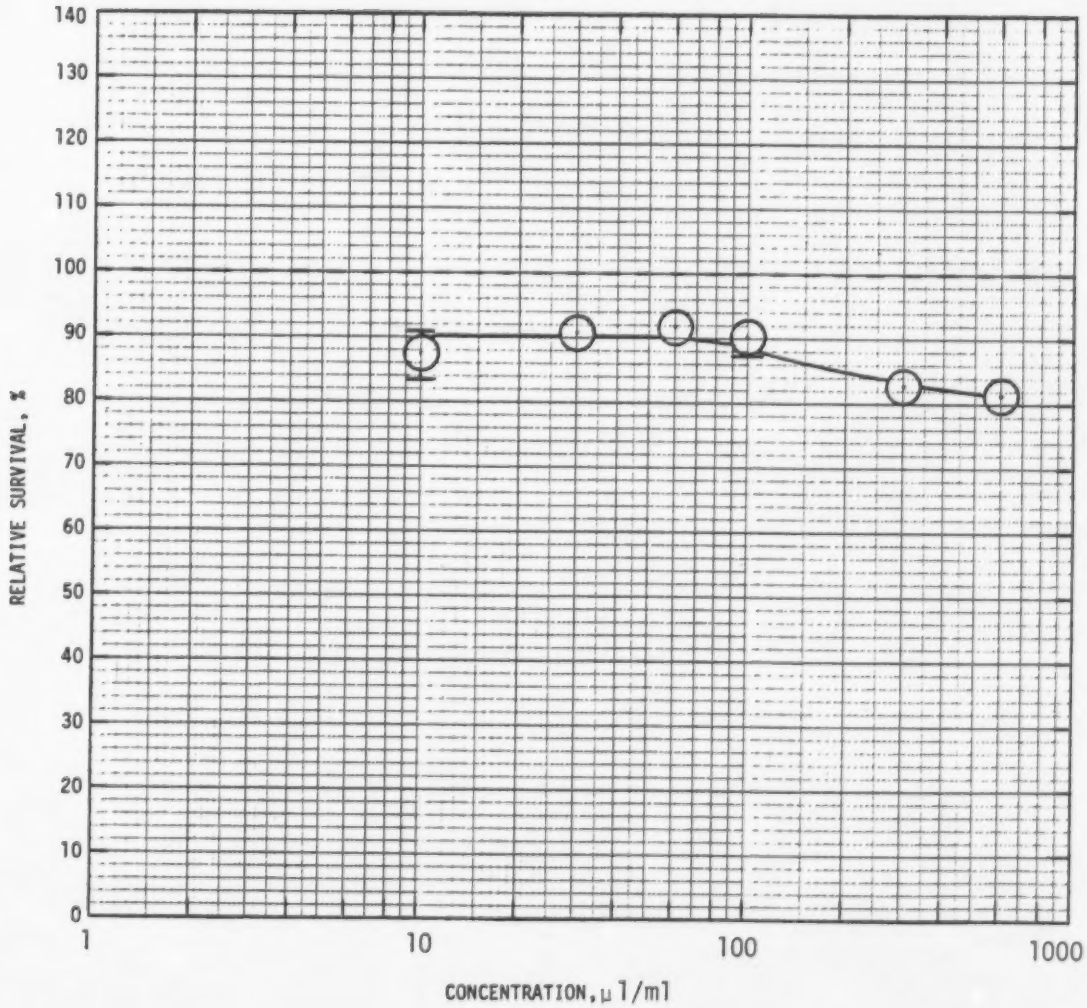


FIGURE 5

RODENT CELL (CHO) CLONAL TOXICITY ASSAY

EC_{50} DETERMINATION

SAMPLE # 4, SOLID FGD SLUDGE

SOLID FORM

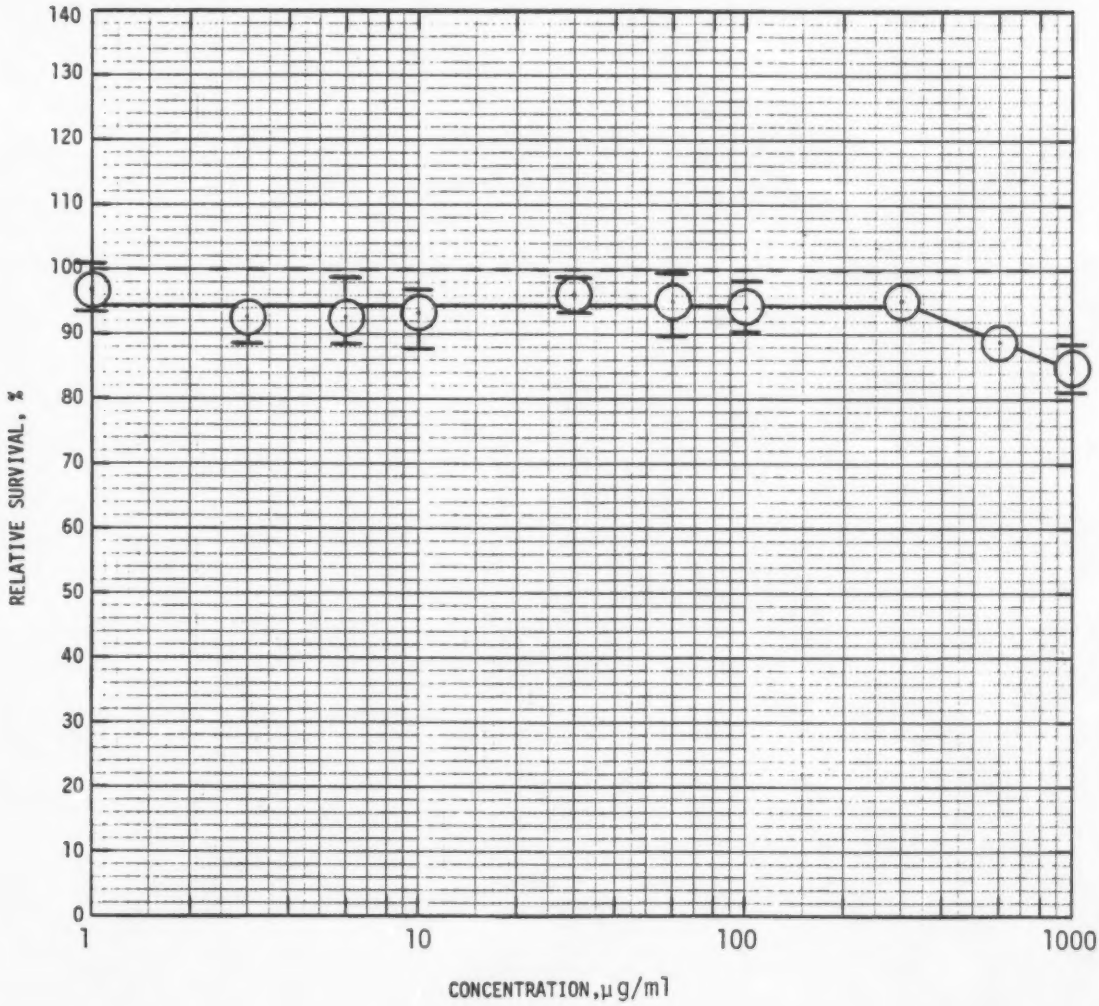


FIGURE 6

RODENT CELL (CHO) CLONAL TOXICITY ASSAY

EC_{50} DETERMINATION

SAMPLE # 4, SOLID FGD SLUDGE

AQUEOUS LEACHATE FORM

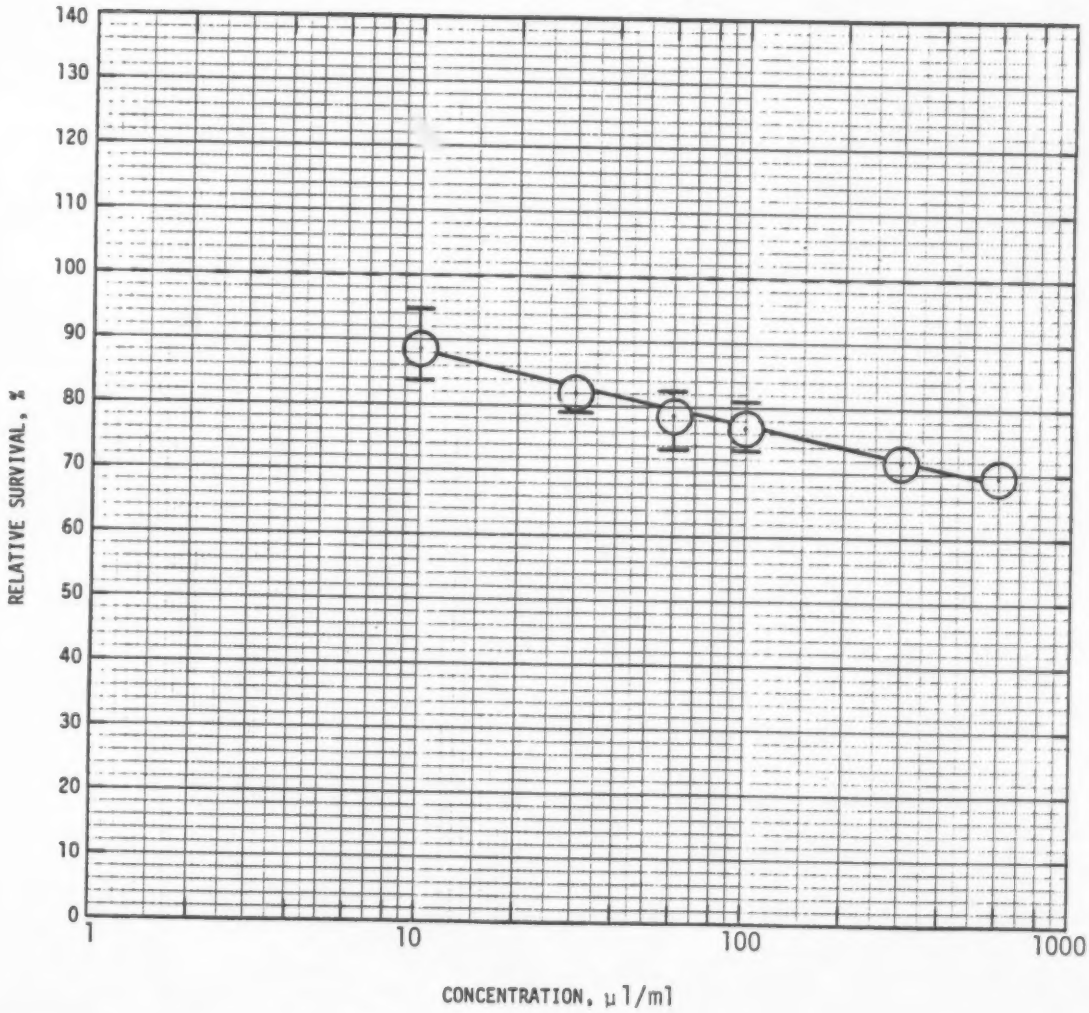


FIGURE 7

RODENT CELL (CHO) CLONAL TOXICITY ASSAY

EC_{50} DETERMINATION

SAMPLE # 5, DBA-FGD SOLIDS

SOLID FORM

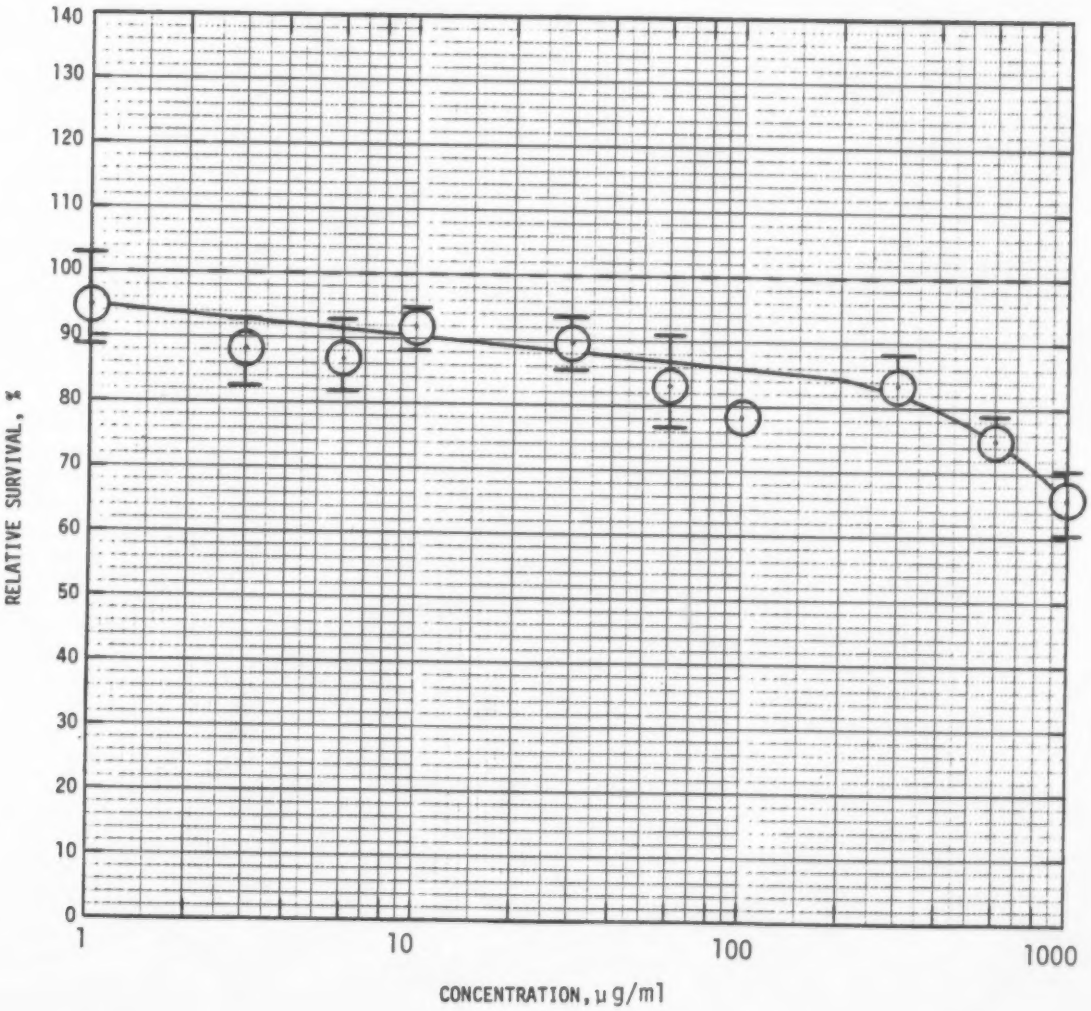


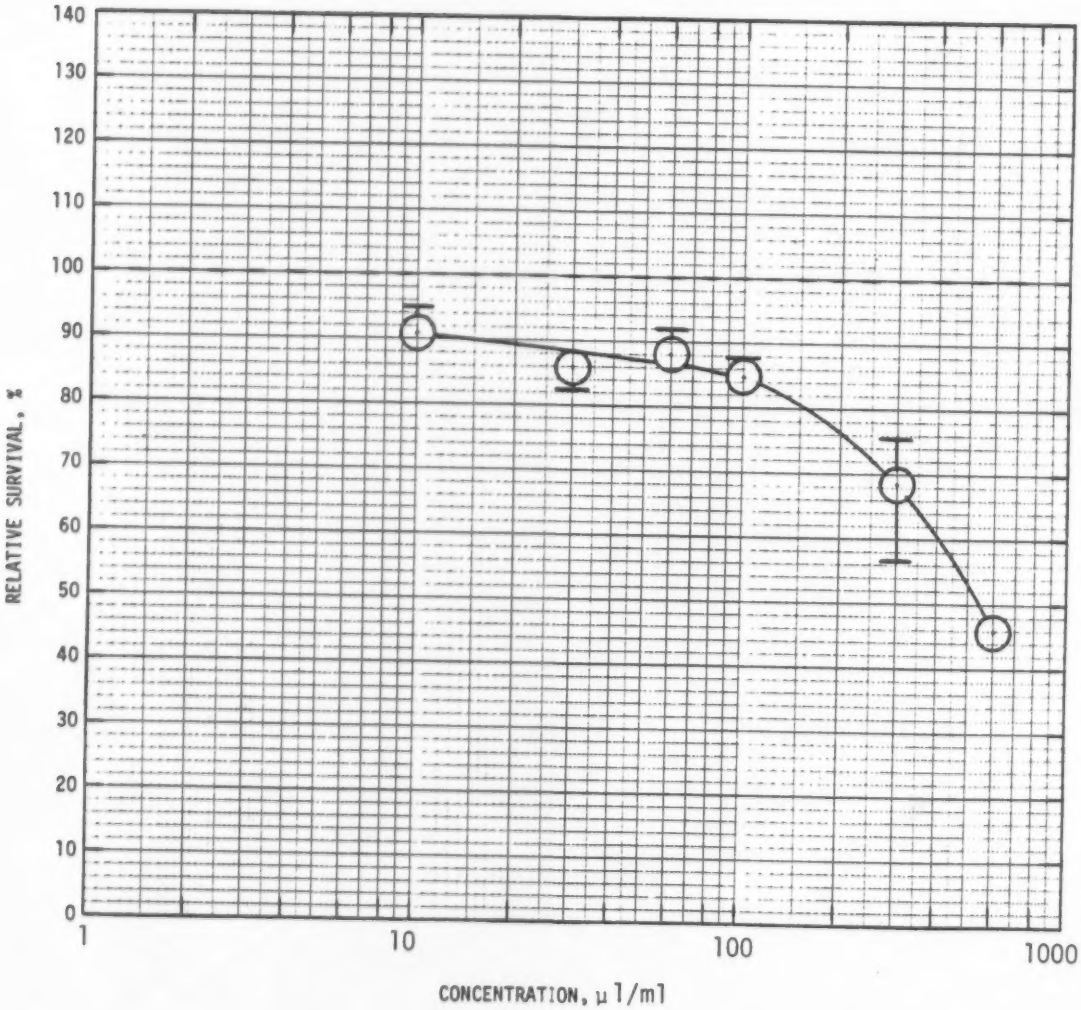
FIGURE 8

RODENT CELL (CHO) CLONAL TOXICITY ASSAY

EC_{50} DETERMINATION

SAMPLE # 5, DBA-FGD SOLIDS

AQUEOUS LEACHATE FORM



VII. ASSAY ACCEPTANCE CRITERIA

The assay is considered acceptable for evaluation of the test results if the following criteria are met:

- The average cloning efficiency of the CHO-K1 cells in the negative controls is 70 percent or greater, but not exceeding 115 percent.

- The distribution of colonies in the treated cultures is generally uniform over the surface of the culture dish.

- The data points for each test concentration critical to the location of the EC_{50} are the averages of at least two treated cultures.

- A sufficient number of test concentrations are available to clearly locate the EC_{50} within a toxicity region as defined under Assay Evaluation Criteria.

- If the EC_{50} value is greater than 1000 μg/ml, 600 μliters of aqueous sample/ml, or 20 μliters of nonaqueous sample/ml, the plotted curve does not exceed 110 percent of the negative control.

VIII. ASSAY EVALUATION CRITERIA

The EC_{50} value represents the concentration of test material that reduces the colony-forming ability of CHO cells to 50% of the vehicle or negative control value. EC_{50} values are determined graphically by fitting a curve by eye through relative survival data plotted as a function of the logarithm of the applied concentration. Each data point normally represents the average of three culture dishes. In order to indicate the variability of the data, the high and low colony counts for each concentration are used to calculate the relative survivals, and the range is shown by a bar at the position of the plotted average. If no bar is shown, the variability was within the size of the symbol. Statistical analysis is unnecessary in most cases for evaluation.

The toxicity of the test material is evaluated as high, moderate, low, or nondetectable according to the range of EC_{50} values defined in the following table:

Toxicity[a]	Solids (EC_{50} in μg/ml)	Aqueous Liquids (EC_{50} in μl/ml)	Nonaqueous Liquids[b] (EC_{50} in μl/ml)
High	<10	<6	<0.2
Moderate	10 to 100	6 to 60	0.2-2
Low	100 to 1000	60 to 600	2-20
Not Detectable	>1000	>600	>20

[a]Evaluation criteria formulated by Litton Bionetics, Inc. for IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests.

[b]Criteria for nonaqueous liquids are tentative and under evaluation. If the organic or solids content is known, the sample is evaluated under the solids criteria.

Another evaluation scheme is proposed for extracts obtained from SASS train gas volumes. The proportion of the total gas volume corresponding to the volume of extract used in the bioassay is calculated and expressed as L/ml of culture medium (or DSCF/ml of culture medium). A criterion of 1000 L/ml is set as the limit for nondetectable toxicity. This gas volume corresponds to the average volume breathed by humans over

a 2-hour period. The subsequent toxicity ranges are defined by 10-fold dilution steps to conform to standard procedure. The toxicity ranges are defined in the following table for liter and dry standard cubic feet units:

Toxicity	EC_{50} In Liters/ml (L/ml)	EC_{50} In Dry Standard Cubic Feet/ml (DSCF/ml)
High	<10	<0.35
Moderate	10-100	0.35-3.5
Low	100-1000	3.5-35
Nondetectable	>1000	>35

IX. REFERENCES

1. Brusick, D.J., et al.: IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests. EPA-600/8-81-024 Litton Bionetics, Inc., Kensington, MD, October 1981, 177 pp.

2. Brusick, D.J.: Level 1 Bioassay Assessment and Data Formatting. EPA-600/7-80-079, Litton Bionetics, Inc., Kensington, MD, April 1980, 100 pp.

3. Brusick, D.J. and Young, R.R.: Level 1 Bioassay Sensitivity. EPA-600/7-81-135, Litton Bionetics, Inc., Kensington, MD, August 1981, pp 52.

GENETICS ASSAY NOS. 6045-6048
LBI SAFETY NOS. 7383-7386

APPENDIX G

TOXIC EVALUATION OF SOLID FGD SLUDGE SAMPLES IN THE EPA LEVEL 1 DAPHNIA MAGNA TOXICITY ASSAY

FINAL REPORT

SUBMITTED TO:

RADIAN CORPORATION
8501 MO-PAC BOULEVARD
P.O. BOX 9948
AUSTIN, TEXAS 78766-0948

PREPARED BY:

BATTELLE COLUMBUS LABORATORIES
505 KING AVENUE
COLUMBUS, OHIO 43201

SUBMITTED BY:

LITTON BIONETICS, INC.
5516 NICHOLSON LANE
KENSINGTON, MARYLAND 20895

LBI PROJECT NO.: 20993

REPORT DATE: FEBRUARY 1982

FINAL REPORT

on

THE TOXICITY OF FGD SLUDGES TO *DAPHNIA MAGNA*

to

LITTON BIONETICS

February 9, 1982

by

D. J. Bean and K. M. Duke

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Battelle is not engaged in research for advertising, sales promotion, or publicity purposes, and this report may not be reproduced in full or in part for such purposes.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
METHODS	1
RESULTS AND DISCUSSION	3
REFERENCES	6

APPENDIX

LABORATORY DATA FOR DAPHNIA MAGNA BIOASSAYS	6

LIST OF TABLES

Table 1.	FGD Sludge Sample Description	2
Table 2.	EC_{50} Values for *Daphnia magna* of FGD Sludge Solids	4
Table 3.	Evaluation Criteria for Level 1 Biological Tests Used to Develop a Relative Ranking of Waste Streams Based on Toxicity	4

BATTELLE'S COLUMBUS LABORATORIES
Columbus, Ohio 43201

Sponsor: Litton Bionetics, Inc.
Kensington, Maryland 20795

Title: The Toxicity of FGD Sludges to *Daphnia magna*

Issue Date:

Report Prepared By: Date:

K M. Duke for DJB — February 16, 1982
David J. Bean
Principal Investigator

Report Approved By: Date:

Kenneth M. Duke — February 16, 1982
Kenneth M. Duke
Program Manager

Dates of Testing: 26 January - 1 February 1982

Litton P. O. Number 109105

Proposal Agreement Number: 526-K-6993

Final Report

on

THE TOXICITY OF FGD SLUDGES TO *DAPHNIA MAGNA*

to

LITTON BIONETICS
Kensington, Maryland

from

BATTELLE
Columbus Laboratories

by

D. J. Bean and K. M. Duke

INTRODUCTION

Bioassays using Daphnia magna as the test organism were conducted to assess the toxicity of four Flue Gas Desulfurization (FGD) sludge solids. This testing was performed to aid in the assessment of the toxicological impacts the waste material may have on the aquatic environment. This work was conducted as part of Battelle's subcontract with Litton Bionetics (LBI Purchase Order No. 109105).

METHODS

The samples tested were solids from FGD sludges (Table 1). Samples were received as dry solids packed in polyethylene bottles. Sample treatment consist of preparation and testing of a leachate from each solid.

Leachate Preparation

Ecological testing of FGD sludge solids samples required preparation of a leachate. The procedure used was basically the ASTM Proposed Method for Leaching of Waste Materials involving agitation of a known weight of solid

TABLE 1. FGD SLUDGE SAMPLE DESCRIPTION

BCL Sample No.	LBI Sample No.	Sample Description
EEC-098	6045	Sample #1 - Solid - FGD Sludge; natural oxidation with fly ash and soil
EEC-099	6046	Sample #2 - Solid - FGD Sludge; natural oxidation with fly ash, soil and adipic acid
EEC-100	6047	Sample #4 - Solids - FGD Sludge; forced oxidation with fly ash, soil and adipic acid
EEC-101	6048	Sample #5 - DBA -FGD Solids with fly ash, soil and di-basic acid

with water and separation of the aqueous phase by filtration.

The solid was weighed and placed in a 1-gallon glass bottle. A volume of water was added equal (in milliliters) to four times the weight (in grams) of the solids. The container was purged with nitrogen to reduce oxidation of the leachate, sealed, and agitated on a drum roller for 48 hours. The solution was allowed to settle and the supernatant decanted and filtered through a 0.45 μm Millipore® membrane filter. Pressurized filtration with oxygen-free nitrogen was used to facilitate this procedure.

Bioassays

EPA Level 1 procedures (Brusick et al. 1980) were used in the biological testing. First instar *Daphnia magna* were used for static acute bioassays. All test organisms were taken from cultures originating from a single female to insure uniformity of strain. Daphnids were cultured in dilution water at test conditions and selected during the log phase of growth of the culture.

The test consisted of six concentrations in a geometric series with each concentration 50 percent of the next higher one. (The maximum applicable dose is 100 percent of a liquid sample). Five organisms were used per replicate with three replicates per concentration and control. The tests were conducted at 19 $\pm$ 2°C with a photoperiod of 16 hours light and 8 hours dark. Specific conductance was measured at the beginning of the test and dissolved oxygen, pH, and temperature were recorded initially and after 48 hours. Immobilization, defined as lack of movement except for minor activity of appendages, was the criterion for effect. Immobilization and abnormal behavior were recorded every 24 hours. Immobilized organisms were removed.

The EC_{50}, the concentration of test material which immobilized 50 percent of the Daphnia magna, and its 95 percent confidence limits were calculated for 24- and 48-hour exposures using probit analysis.

The probit method of data analysis uses the probit transformation and the maximum likelihood curve-fitting technique. This method assumes that the concentration-mortality curve is linear. Stephan (1977) recommends the logarithmic transformation of concentration data to help assure this linearity. However, our analysis uses the probit transformation both with and without the log transformation of the concentration data. The results are examined to ascertain which method gives the best fit to the probit curve. The appropriate EC_{50} is then reported.

The probit method of analysis also allows the calculation of 95 percent confidence limits about the EC_{50}. While the confidence limits do give information about the precision of the individual EC_{50} estimate they do not indicate the reproducibility or repeatability of acute mortality tests done at different times or in different laboratories (Stephan, 1977).

RESULTS AND DISCUSSION

All four FGD sludge samples were toxic to Daphnia magna (Table 2). Survival at each test concentration in addition to the other parameters measured are tabulated in the Appendix.

TABLE 2. EC_{50} VALUES FOR DAPHNIA MAGNA OF FGD SLUDGE SOLIDS

Sample	24-Hour EC_{50}[a] Percent Concentration	48-Hour EC_{50}[a] Percent Concentration	Relative[b] Toxicity
6045	73.3 (40.5-106.1)	44.9 (32.1-57.8)	M
6046	16.2 (12.6-19.8)	15.0 (11.8-18.2)	H
6047	None--100% survival at 100% test concentration	76.6 (56.0-104.8)	M(L)[c]
6048	69.3 (54.5-84.0)	69.3 (54.5-84.0)	M

[a]95% confidence interval in parentheses

[b]Ranking based on Table 3

[c]EC_{50} within 5% of border line

TABLE 3. EVALUATION CRITERIA FOR LEVEL 1 AQUATIC BIOLOGICAL TESTS USED TO DEVELOP A RELATIVE RANKING OF WASTE STREAMS BASED ON TOXICITY[(a)]

Relative Sample Toxicity - EC_{50}			
High	Moderate	Low	Not Detectable
<20	20-75	75-100	>100

[(a)]Brusick, et al., 1980.

Results indicate that three of the four FGD solids were moderately toxic to Daphnia according to the toxicity categories for aquatic ecological assays. Sample 6046 was ranked highly toxic. This sample was similar to 6045 except for the addition of adipic acid.

An examination of the raw data (Appendix) show that in all cases, the specific conductance of the test solutions, a measure of ion concentration of the water and an indicator of hardness, increased substantially as the percent concentration of leachate increased. This increase was most likely a contributing factor to the toxicity of the FGD sludge solids, as Daphnia magna are sensitive to this parameter. Sample 6046 showed the largest increase in specific conductance, as well as a significant increase in pH with increasing leachate concentration. In the 25, 50 and 100% concentration the pH was outside the generally accepted tolerance range of 6-10 for Daphnia magna.

REFERENCES

ASTM. Proposed Method for Leaching of Waste Materials ASTM, 1916 Race Street, Philadelphia, Pennsylvania, 19103.

Brusick, D. J., R. R. Young, C. Hutchinson, A. G. Dilkar and T. A. Gezo. IERL-RTP Procedures Manual-Level 1 Environmental Assessment Biological Tests. Draft Report to U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C., 1980, pp 158.

Stephan, C. E., "Methods for Calculating an LC50", in Aquatic Toxicology and Hazard Evaluation, ASTM STP 634, F. L. Mayer and J. L. Hamelink, (Eds.), American Society for Testing and Materials Philadelphia, 1977.

APPENDIX

LABORATORY DATA FOR *DAPHNIA MAGNA* BIOASSAYS

DAPHNIA STATIC BIOASSAY RECORD SHEET

Material being tested EEC-099 Source Litton

Source of dilution H_2O RO well mix 1-22-82 Charge # N0930-7502

Test species Daphnia magna # Individuals/ % waste 15

Technician RJa Date 1-28-82 Starting hour 6:30 pm

	Start																							
% Waste		100	100	50	50	50	50	25	25	25	12.5	12.5	12.5	6.25	6.25	6.25	3.125	3.125	3.125	Control				
Rep #		3	2	1	3	2	1	3	2	1	3	2	1	3	2	1	3	2	1	3	2	1		
DO		8.6	8.6	8.6	9.2	9.2	9.[illegible]	9.8	9.8	9.8	9.7	9.7	9.8	9.8	9.8	9.9	9.9	10.0	10.1	10.2	10.4	10.4		
Temp.		18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18		
pH		12.2	12.2	12.2	12.0	12.0	12.0	11.4	11.4	11.4	[illegible]	10.4	10.4	9.6	9.6	9.6	9.1	9.1	9.1	8.0	8.0	8.0		
Specific Conductance		7500	7500	7500	3000	[illegible]	2700	1050	1000	1000	[illegible]	[illegible]	[illegible]	575	575	600	600	625	600	575	575	550		
	24 hrs																							
Number Surviving		0	0	0	0	0	0	0	0	0	5	5	4	5	5	4	5	4	5	5	5	5		
% Survival		0	0	0	0	0	0	0	0	0	100	100	80	100	100	80	100	80	100	100	100	100		
	48 hrs																							
Number Surviving		0	0	0	0	0	0	0	0	0	5	4	3	5	5	4	5	4	5	5	5	5		
% Survival		0	0	0	0	0	0	0	0	0	100	80	60	100	100	80	100	80	100	100	100	100		
DO		9.6	9.8	9.7	9.7	9.8	9.7	9.7	9.8	9.8	10	10	9.9	9.9	10	10	10	10	10	10	10	9.9		
Temp.		18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18		
pH		11.25	11.55	11.55	10.5	10.55	10.45	9.9	10.3	9.9	9.15	9.1	9.15	8.55	8.55	8.55	8.45	8.45	8.45	8.6	8.6	8.6		

Remarks:

DAPHNIA STATIC BIOASSAY RECORD SHEET

Material being tested EEL-160 Source [illegible]

Source of dilution H_2O Power mix Charge # [illegible]-7502

Test species [illegible] # Individuals/ % waste 15

Technician [illegible] Date 1-26-82 Starting hour 5:00 pm

	Start																						
% Waste			100	100	100	100	100	75	25	25	12.5	12.5	12.5	6.25	6.25	3.13	3.13	3.13	3.13	Control			
Rep #			2	1	3	2	1	3	2	1	3	2	1	3	2	1	3	2	1	3	2	1	
DO			8.5	8.5	8.6	8.5	8.4	8.5	8.4	8.4	8.5	8.5	8.4	8.4	8.4	8.5	8.6	8.6	8.6	8.6	8.4	8.6	
Temp.			18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	
pH			7.4	7.4	7.5	7.6	7.6	7.6	7.6	7.5	7.6	7.6	7.6	7.6	7.6	7.6	7.6	7.5	7.4	7.5	7.5	7.5	
Specific Conductance			2175	2275	1425	1400	1400	1025	1075	1075	550	525	800	725	725	700	675	675	150	600	600	575	
	24 hrs																						
Number Surviving			5	5	5	4	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
% Survival			100	100	100	80	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	
	48 hrs																						
Number Surviving			1	2	5	4	3	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
% Survival			20	40	100	80	60	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	
DO			8.4	8.4	8.4	8.4	8.4	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.4	8.4	
Temp.			18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	
pH			7.7	7.7	8.1	8.1	8.1	8.2	8.2	8.2	8.3	8.3	8.3	8.3	8.3	8.3	8.3	8.2	8.2	8.2	8.2	8.2	

Remarks: 1. one caught in surface tension - no movement